

Prediction of Partition Coefficients of Organic Compounds for SPME/PDMS

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Abstract. The partition coefficients of 51 organic compounds between SPME/PDMS and gas were compiled from the literature sources in this study. The effect of physicochemical properties and descriptors on the partitioning process of partition coefficients was explicated by the correlation analysis. The PDMS-gas partition coefficients were well correlated to the molecular weight of organic compounds ($r=0.832$, $p<0.05$). An empirical model, consisting of the molecular weight and the polarizability, was developed to appropriately predict the partition coefficients of organic compounds. The empirical model for estimating the PDMS-gas partition coefficient will contribute to the practical applications of the SPME technique.

1 Introduction

Solid phase microextraction (SPME) is a solvent-free sample preparation technique. Polymeric materials, such as polydimethylsiloxane (PDMS), are coated onto the outer layer of the fused silica rod of the SPME device. According to the principle of partitioning, the analyte is adsorbed from the sample matrix onto the coating stationary phase. The concentrated extract is then transferred to an instrument, such as gas chromatography, for thermal desorption and analysis. Prior to using the SPME technique for sampling and analysis, the first step is to select the appropriate polymer as the SPME fiber and to determine the equilibrium extraction time for SPME, which is primarily based on the partition

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coefficient of the analyte between the SPME fiber and the sample matrix.

The objective of this study is to develop predictive equations for the partition coefficients of a variety of organic compounds in gas onto SPME/PDMS. This was achieved by using the PDMS-gas partition coefficients retrieved from the literature and relating them to their physicochemical properties and molecular descriptors, such as molecular connectivity index ($^1\chi$), water solubility (WS), molecular weight (MW), octanol-water partition coefficient ($\log K_{ow}$), and polarizability (Φ). The results of this study can facilitate the application of the SPME technique.

2 Method

In this study, the PDMS-gas partition coefficients K_{fg} for alkanes and aromatic hydrocarbons was compiled from the literature published by Dr. Pawliszyn [1]. As shown in Table 1, the values of K_{fg} ($n=51$) exhibit a wide range from 157 (for benzene) to 95,700 (for 3,3-dimethyloctane).

Table 1 the Training Set Of Pdms-Gas Partition Coefficients And Physico-Chemical Descriptors

Compound	K_{fg}	$^1\chi$	Φ	I	$M_w(\text{g/mol})$ e)	WS (mg/L)	$\log K_{ow}$
3-Methylpentane	159	2.80 8	1.7 82	0	86.18	17.9	3.6
2,4-Dimethylpentane	262	3.12 6	2.1 19	0	100.2	5.5	3.63
2,2,3-Trimethylpentane	569	3.48 14	2.4 56	0	114.20	2.40	4.09
2,3-Dimethylhexane	968	3.68 08	2.4 56	0	114.23	9.20	4.12
2-Methylheptane	993	3.77 01	2.4 56	0	114.23	7.97	4.20
4-Methylheptane	1,06 0	3.80 80	2.4 56	0	114.23	7.97	4.20
3-Methylheptane	1,09 0	3.80 80	2.4 56	0	114.23	0.792	4.20
3-Ethylhexane	990	3.84 59	2.4 56	0	114.23	7.97	4.20
2,5-Dimethylheptane	1,97 0	4.16 39	2.7 93	0	126.28	3.11	4.61
3,5-Dimethylheptane	1,96 0	4.20 18	2.7 93	0	128.26	3.11	4.61
3,3-Dimethylheptane	2,09 0	4.12 14	2.7 93	0	128.26	2.90	4.65

2,3-Dimethylheptane	2,390	4.1808	2.793	0	128.26	3.37	4.61
3,4-Dimethylheptane	2,420	4.2187	2.793	0	128.26	3.11	4.61
2-Methyloctane	2,600	4.2701	2.793	0	128.26	2.87	4.69
3-Methyloctane	2,890	4.3080	2.793	0	128.26	2.87	4.69
3,3-Diethylpentane	2,610	4.2428	2.793	0	128.00	2.90	4.65
2,2-Dimethylpentane	4,320	3.0607	2.119	0	100.20	4.40	3.67
3,3-Dimethylpentane	5,050	3.1214	2.119	0	100.20	5.92	3.67
2,3-Dimethylpentane	6,100	3.1808	2.119	0	100.20	5.25	3.63
2-Methylnonane	6,690	4.7701	3.130	0	142.28	0.899	5.18
3-Methylnonane	7,100	4.8080	3.130	0	142.28	0.97	5.18
Benzene	301	1.9998	0.165	1	78.11	1790.0	0.213
Toluene	818	2.4106	0.502	1	92.14	526.00	2.73
Ethylbenzene	2,070	2.9713	0.839	1	106.17	169.00	3.15
m-Xylene	2,090	2.8214	0.839	1	106.00	161.00	3.20
p-Xylene	2,500	2.8214	0.839	1	106.16	162.00	3.15
o-Xylene	2,900	2.8273	0.839	1	106.00	178.00	3.12
Isopropylbenzene	3,880	3.3541	1.176	1	120.19	61.30	3.66
n-Propylbenzene	5,040	3.4713	1.176	1	120.19	52.20	3.69
1-Methyl-3-Ethylbenzene	4,750	3.3821	1.176	1	120.19	40.00	3.98
1-Methyl-4-Ethylbenzene	6,230	3.3821	1.176	1	120.19	94.90	3.63
1,3,5-Trimethylbenzene	6,480	3.2322	1.176	1	120.19	48.20	3.42
Isobutylbenzene	8,360	3.8272	1.513	1	134.22	10.10	4.68
sec-Butylbenzene	8,590	3.8920	1.513	1	134.22	17.60	4.57
1-Methyl-3-Isopropylbenzene	10,100	3.7649	1.513	1	134.22	42.50	4.50
1-Methyl-4-Isopropylbenzene	10,200	3.7649	1.513	1	134.22	23.40	4.10

1-Methyl-3-n-Propylbenzene	13,200	3.8821	1.513	1	134.22	9.09	4.67
1,2-Dimethyl-4-Ethylbenzene	17,400	3.7988	1.513	1	134.22	12.70	4.50
1,3-Dimethyl-2-Ethylbenzene	18,100	3.8047	1.513	1	134.22	19.60	4.28
1,2-Dimethyl-3-Ethylbenzene	20,000	3.8047	1.513	1	134.22	17.40	4.34
1,2,4,5-Tetramethylbenzene	24,700	3.6548	1.513	1	134.22	3.48	4.00
2-Methylbutylbenzene	24,100	3.7877	1.850	1	148.24	12.70	4.43
n-Pentylbenzene	34,500	4.4713	1.850	1	148.24	3.37	4.90
1,3,5-Triethylbenzene	67,300	4.9143	2.187	1	162.27	0.014	5.11
1,2,4-Triethylbenzene	75,600	4.9202	2.187	1	162.27	2.90	5.11
n-Hexylbenzene	90,100	4.9713	2.187	1	162.20	0.902	5.52
1-Methyl-3-Isopropylbenzene	10,100	3.7649	1.513	1	134.22	42.50	4.50
1-Methyl-4-Isopropylbenzene	10,200	3.7649	1.513	1	134.22	23.40	4.10
1-Methyl-3-n-Propylbenzene	13,200	3.8821	1.513	1	134.22	9.09	4.67
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1-Methyl-3-n-Propylbenzene	13,200	3.8821	1.513	1	134.22	9.09	4.67

The polarizability and molecular connectivity index were used to represent the interactions between the analyte and PDMS coating. As shown in Eq. (1), the polarizability Φ was determined by the addition of atom/bond contribution factors [2,3].

$$\Phi = \sum F_i \times (\text{number of atom / bond}) \quad (1)$$

where F_i is the contribution factors indicated in Table 2 .

Table 2. Contribution factors for the calculation of polarizability.

Atom/bond	Contribution factor	Atom/bond	Contribution factor
Carbon	0.577	Iodine	0.407
Hydrogen*	-0.120	Fluorine	-0.570
Oxygen	-0.825	Cycle	-0.952
Hydroxyl	-3.701	Double bond	-0.859
Chlorine	-0.187	Triple bond	-0.109
Bromine	-0.222	-	-

Data was obtained from Nirmalakhandan and Speece [2]; *Attached to carbon atoms only.

The molecular connectivity index is a topological descriptor of molecular structure based on a count of skeletal atom groupings of a chemical compound [4,5]. For each atom of a molecule, a δ value is assigned as the difference between the number of valence electrons and the number of hydrogen atoms attached to that atom. The first-order connectivity index was calculated as [1,6,7]:

$${}^1\chi = \sum_{q=1}^n (\delta_i \delta_j)^{-0.5} \quad (2)$$

Where δ_i and δ_j are the δ values of two adjacent atoms i and j , respectively; and n is the number of bonds in the molecule.

3 Results and Discussion

As presented in Table 2, K_{fg} was found to correlate best with the molecular weight of organic compounds ($r=0.832$, $p<0.05$). Therefore, the molecular weight can be a good basis to understand the partition between SPME/PDMS and organic compounds in the gas. Table 3 indicates that K_{fg} was positively correlate to the $\log K_{ow}$ ($r=0.550$, $p<0.05$) and the molecular connectivity index ($r=0.581$, $p<0.05$) of organic compounds. Therefore, the

partition of organic compounds between PDMS and the gaseous matrix was dependent on their polarity and structure of molecular.

Table 3 Correlation analysis of K_{fg} for the training set

Descriptor	Correlation
M_W	$\log K_{fg} = -0.052 + 0.029 M_W$ ($r=0.832, p<0.05$)
$^1\chi$	$\log K_{fg} = 1.139 + 0.594^1\chi$ ($r=0.581, p<0.05$)
$\log K_{ow}$	$\log K_{fg} = 1.297 + 0.539 \log K_{ow}$ ($r=0.550, p<0.05$)
Φ	$\log K_{fg} = 3.673 - 0.078\Phi$ ($r=-0.085, p>0.05$)
WS	$\log K_{fg} = 3.569 - 0.0001 WS$ ($r=-0.257, p<0.05$)

Due to the polarity of compounds is affected by hydrogen bond, molecular structure and symmetry, we grouped K_{fg} into alkane and aromatic hydrocarbons. It was found that the correlation between molecular descriptors and K_{fg} was better. The K_{fg} of alkane and aromatic hydrocarbon was well correlated with $^1\chi$ ($r=0.609, r=0.961$), Φ ($r=0.614, r=0.981$) and M_W ($r=0.615, r=0.981$).

The best predictive model for K_{fg} was obtained through the multiple regression analysis. Based on the stepwise regression with 95% confidence limits, the multiple regression analyse of K_{fg} is presented as Eq. (3).

$$\log K_{fg} = 0.117 - 0.353\Phi + 0.034M_W \quad (3)$$

As shown in Fig. 1, there was a good agreement ($r=0.908$) between the experimental K_{fg} and those determined by Eq. (3), and there was no significant difference with a statistical analysis of the t-test ($p<0.05$). Therefore, the predictive model of Eq. (3) can be employed to estimate K_{fg} for SPME/PDMS to extract the analyte from the gaseous sample.

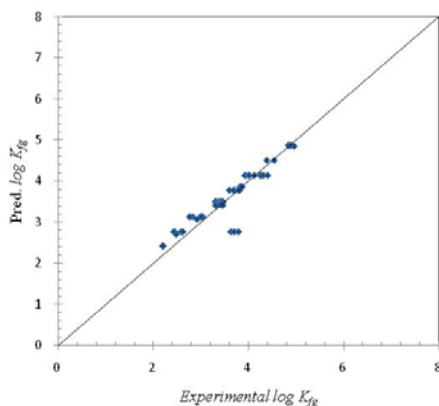


Fig. 1 Comparison of K_{fg} between the experimental data and the predictive model.

4 Conclusion

According to the single-parameter model analyses, the PDMS-gas partition coefficients were proportional to the molecular weight, molecular connectivity index, and octanol-water partition coefficient of organic compounds, while an inversely proportional trend was observed between K_{fg} , and polarizability as well as the water solubility. K_{fg} was dependent on the molecular weight of the organic compounds most. Based on the results of multiple regression analyses, a correlation for K_{fg} was developed using the molecular weight and the polarizability, indicating a good agreement ($r=0.908$) between the experimental data and the predicted K_{fg} . The empirical model developed in this work is more versatile than current available correlations. In order to broaden the predictive abilities, however, future work should be conducted to calculate K_{fg} using the empirical model for a variety of organic compounds.

References

1. Pawliszyn, J., "Solid Phase Microextraction – Theory and Practice", 1997, Wiley-VCH, New York.
2. Nirmalakhandan, N.N.; Speece, R.E. QSAR model for predicting Henry's constant. *Environ. Sci. Technol.* 1988, 22, 1349–1357.
3. Horvath, A.L. *Halogenated Hydrocarbons*; Dekker: New York, NY, USA, 1982.
4. Kier, L.B.; Hall, L.H. *Molecular Connectivity in Structure—Activity Analysis*; Wiley: Chichester, UK, 1986.
5. Randic, M. On characterization of molecular branching. *J. Am. Chem. Soc.* 1975, 97, 6609–6615.
6. Nirmalakhandan, N.N.; Speece, R.E. QSAR model for predicting Henry's constant. *Environ. Sci. Technol.* 1988, 22, 1349–1357.
7. Zhao, H.; Zhang, Q.; Chen, J.; Xue, Z.; Liang, X. Prediction of octanol-air partition coefficients of semivolatile organic compounds based on molecular connectivity index. *Chemosphere* 2005, 59, 1421–1426.