

## Measurement and Prediction of Hexadecanol/Air Partition Coefficients for Numerous Organic Solutes

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### Introduction

The environmental fate of organic pollutants is strongly influenced by their distribution between the atmosphere and various liquid and solid phases. Partition coefficients between organic solvents and the gas phase,  $K_{S/A}$  provide important descriptors for studying solute-solvent molecular interactions and environmental pathways<sup>1,2</sup>. The alcohols occupy a somewhat peculiar position in the rank of solvents because, like water, they can form hydrogen bonds, but with respect to other properties they are much more similar to organic solvents<sup>3</sup>. In this study, hexadecan-1-ol was chosen to represent the solubility properties of the long-chain alcohols, which affords the possibility to compare its solvation properties with those of other commonly used model solvents.

Experimental measurements of partitioning characteristics are necessary, but also time consuming. Therefore, reliable estimates of phase partitioning are essential for accurate predictions of the environmental fate of organic chemicals. Whereas simple empirical one-parameter linear free energy relationships (SP-LFERs) involving such properties are commonly used to interpret or predict environmental partitioning equilibria<sup>4,5</sup>, it has been pointed out that the predictive power of such SP-LFERs is limited because a single parameter is incapable to describe appropriately all the molecular interactions that contribute to environmental phase partitioning processes<sup>6</sup>.

So called linear solvation energy relationships (LSER), an estimation method advocated by Abraham and others, is one of the most useful poly-parametric linear free energy relationship (PP-LFER) approaches for the analysis and prediction of solute partitioning in chemical and biochemical systems. It has been used to correlate and predict solute properties in numerous systems<sup>7</sup>. Breivik & Wania<sup>8</sup> have argued that LSER-based environmental fate models are applicable to a much wider range of organic substances, in particular those with polar functional groups. For processes involving gas to condensed phase transfer, the LSER equation takes the form:

$$\log SP = c + rR_2 + s\pi_2^H + a\sum\alpha_2^H + b\sum\beta_2^H + l\log L_{16} \quad (1)$$

The dependent variable,  $\log SP$ , is the solvation property of interest, and  $R_2$ ,  $\pi_2^H$ ,  $\sum\alpha_2^H$ ,  $\sum\beta_2^H$  and  $\log L_{16}$  are solute descriptors representing the excess molar refraction, dipolarity/polarizability, hydrogen bond acidity, hydrogen bond basicity, and the gas-hexadecane partition coefficient, respectively. These descriptors quantify the tendency of a solute to undergo various solute-solvent interactions and the energy required to form the cavity that will accommodate a solute. The coefficients  $r$ ,  $s$ ,  $a$ ,  $b$  and  $l$  in eq. (1), called system constants, specify the molecular interaction within the two-phase system.

Li & Carr<sup>9</sup> indicated that system constants for capacity factors on a series of GC columns are linearly related with reciprocal temperature  $T$ :

$$X = X_A + X_B / T \quad (2)$$

where  $X$  stands for a system constant, and  $X_A$  and  $X_B$  are the intercept and slope of the regression, respectively<sup>9</sup>.

In this project, we experimentally determined hexadecan-1-ol/air partition coefficient ( $K_{16OH}$ ) for a large number of organic solutes, derived temperature dependent LSER system constants from the data, and performed comparisons

with other prediction methods.

## Methods

The phase ratio variation (PRV) method based on headspace gas chromatography was modified to allow the determination of equilibrium partition coefficients involving a solid matrix and multiple solutes. This method measures the gas phase concentration in a series of vials containing different volumes of the same solution. The partition coefficient can be expressed as a function of the vapor phase concentrations at equilibrium and the phase ratio, i.e. the volume ratio of the vapour phase to solvent phase.<sup>10</sup> The modified experimental procedure, which uses mass and density of the solvent instead of volume to determine the phase ratio, was applied to measure the  $K_{16OH}$  of numerous organic solutes as a function of temperature between 70 to 110°C. The  $K_{16OH}$  values at 25°C were derived from a regression of  $\log K_{16OH}$  vs. reciprocal temperature. LSER analysis was used to characterise the solvent properties. Multiple linear regressions were performed using SPSS 12.0 for windows (SPSS Inc.). Resistant regression (least median square method) used in the analysis of temperature dependence was conducted using R 2.0.1 (The R development core team).

## Results and Discussions

The measured partitioning data at the experimental temperatures were regressed against LSER solute descriptors taken from the literature<sup>11-14</sup>. The correlation between  $\pi_2^H$  and  $\log K_{16OH}$  for the compounds of interest was insignificant at all experimental temperatures and this parameter was thus excluded from further regressions. The other solute descriptors are all entered without further consideration to their significance. The system constants obtained by multiple linear regression analysis are given in Table 1. These system constants reveal that the gas-hexadecan-1-ol partition coefficients are strongly correlated to a solute's  $\log L_{16}$ , which means that the  $K_{16OH}$  is strongly affected by the cavity effect and dispersive solute/solvent interactions. The solute hydrogen acidity and basicity also show a significant relation to  $K_{16OH}$ , confirming that hexadecan-1-ol serves as both hydrogen donor and acceptor during the partitioning process. The relative size of the system constants relays information on the relative importance of different types of solute/solvent interactions. They were as follows: the strength of the interaction decreases from cavity effect, hydrogen bond effect (including  $\sum \alpha_2^H$  and  $\sum \beta_2^H$ ,  $a > b$ ), solute/solvent  $s/p$  electron pair interaction to solute/solvent dipolarity/ polarizability interaction, i.e.,  $l > a > r \approx b > s$  (is not significant).

Table 1. LSER system constants for the hexadecan-1-ol/air system at various temperatures.

	c	l	a	r	b	R <sup>2</sup>
70°C	0.3334	0.6357	1.7532	0.3842	0.438	0.949
80°C	0.3201	0.6083	1.6045	0.2946	0.4326	0.952
90°C	0.2155	0.5932	1.4078	0.3387	0.4099	0.943
100°C	0.3612	0.527	1.4148	0.2825	0.4157	0.947
110°C	0.3017	0.5218	1.6634	0.2662	0.1067	0.884

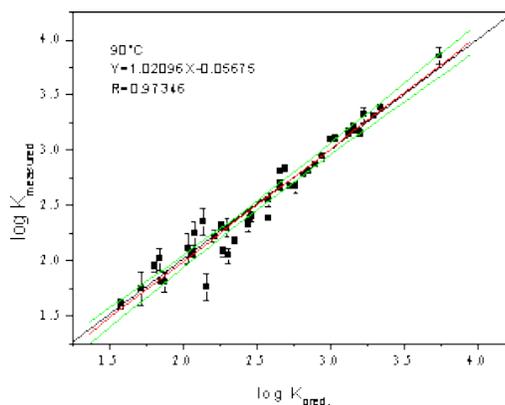


Fig. 1. Comparison of observed and LSER-predicted  $\log K_{16OH}$  values at 90°C.

Figure 1 shows that the partitioning coefficients at 90 °C are well described by the LSER equation. The data points are close to the diagonal 1:1 line, and most of the data points are well within the 95% confidence limit.

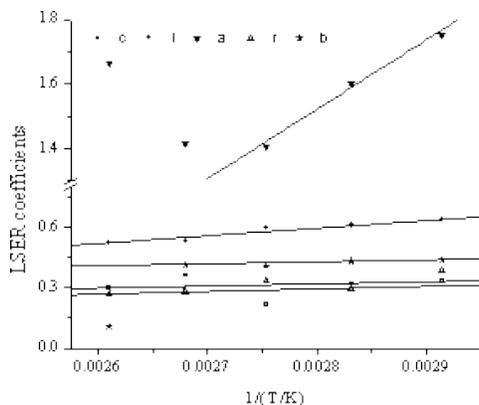
Fig. 2. Temperature dependence of LSER system constants for  $\log K_{16OH}$ .

Table 2 Temperature dependence of the LSER coefficients from Least Median Square regression.

	c	l	a	r	b
$X_B$	104.094	374.697	2151.9	128.102	95.237
$X_A$	0.02768	-0.4545	-4.503	-0.06449	0.1617

Figure 2 displays the temperature dependence of the system constants. Most system constants conform to eq. (2) and show linearity with  $1/T$ . However, some points, especially those measured at 110 °C, deviate significantly from the linear trends. The LSER equation at 110 °C was based on fewer chemicals and  $\sum \beta_2^H$  was not significant in this equation. To overcome this outlier problem, a least median square technique was used to draw the regression. The fitting results are given in Table 2. From those temperature regression equations, the LSER equation for  $\log K_{16OH}$  at 25°C can be estimated:

$$\log K_{16OH} @ 25^\circ C = 0.3768 + 0.3652R_2 + 2.7145 \sum \alpha_2^H + 0.4811 \sum \beta_2^H + 0.80221 \log L_{16} \quad (3)$$

Figure 3 compares the system constants for  $K_{16OH}$  with those obtained for other alcohols by subtracting the system constants for different normal alcohols from those for water and plotting the difference against carbon number <sup>3</sup>. This figure clearly shows how the solvation properties of aliphatic alcohols compared with water change with increasing carbon chain length. Compared with water, only the constant c and the l coefficient adopt positive numbers, whereas all the other coefficients are negative. That suggests that the cavity effect and the solute/alcohol dispersion interaction in hexadecan-1-ol are much stronger than that in water. The figure also shows that the differences between the solvation characteristic of the normal alcohols become less significant with increasing length of the aliphatic chain. Non-linear exponential curves of the type ( $y = y_0 + A_1 e^{x/n}$ ) were fitted to the data in Fig. 3. The estimated LSER regression for hexadecan-1-ol estimated from these curves is as follows.

$$\log K_{16OH} = -0.06298 - 0.1548R_2 + 0.4246\pi_2^H + 3.4932 \sum \alpha_2^H + 0.9396 \sum \beta_2^H + 0.89761 \log L_{16} \quad (4)$$

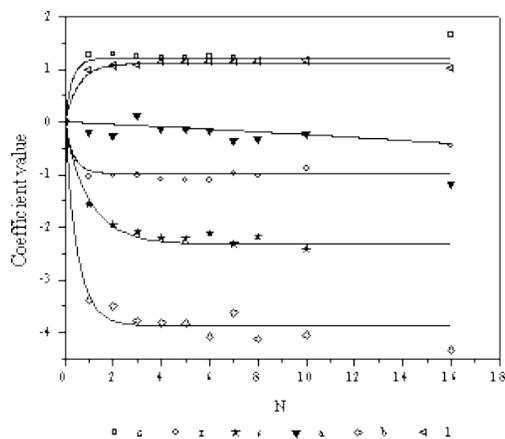


Fig. 3. Comparison of the coefficients in eq. (3) with those for other alkanols based on the difference to system constants for gas-water partitioning. N represent the carbon number, for water, N=0

Figure 3 also includes the system constants for  $K_{16OH}$  as given in eq. (3). Considering the experimental and regression uncertainty, results from this study are consistent with the extrapolated results from previous research<sup>3</sup>. Only the a and r coefficients show relatively large discrepancies.  $K_{16OH}$  values predicted with eqs. (3) and (4) were compared and found to agree well with each other. A paired two sample ttest revealed no significant difference between the two sets of prediction ( $t=1.884$ ,  $p=0.067$ ).

Further comparing the system constants for  $\log K_{16OH}$  and  $\log K_{OA}$  (octanol-air partition coefficient) with that for the plant cuticle/air system<sup>7</sup>, we found that the regression coefficients l, a, b and r in eq. (4) resemble those for plant cuticles more closely. This indicates that, as a reference solvent, hexadecan-1-ol may have solvation characteristics which are relatively more similar to those of natural organic matter than octan-1-ol.

### Acknowledgements

We are grateful for funding from the Natural Sciences and Engineering Research Council (NSERC) of Canada.

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