**Quantitative Structure-Retention Relationship Modeling of Gas Chromatographic Retention Times Based on Thermodynamic Data**

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**Abstract**

Thermodynamic parameters of ∆H(T0), ∆S(T0), and ∆Cp for 156 compounds comprising alkanes, alkyl halides and alcohols were determined for a 5% phenyl 95% methyl stationary phase. The determination of thermodynamic parameters relies on a Nelder-Mead simplex optimization to rapidly obtain the parameters. Two methodologies of external and leave one out cross validations were applied to assess the robustness of the estimations of thermodynamic parameters. The largest absolute errors in predicted retention time across all temperature ramps and all compounds were 1.5 and 0.3 s for external and internal sets, respectively.

The possibility of an *in silico* extension of the thermodynamic library was tested using a quantitative structure-retention relationship (QSRR) methodology. The estimated thermodynamic parameters were utilized to develop QSRR models. Individual partial least squares (PLS) models were developed for each of the three classes of the molecules. R2 values for the test sets of all models across all temperature ramps were larger than 0.99 and the average of relative errors in retention time predictions of the test sets for alkanes, alcohols, and alkyl halides were 1.8%, 2.4%, and 2.5%, respectively.

**1. Introduction**

Optimization of gas chromatographic separations requires careful attention to a number of important variables and their interactions. When using comprehensive multidimensional gas chromatography (GC×GC) to separate a complex mixture, true optimization of the separation conditions is more elaborate and time-consuming than for one-dimensional separations of comparatively simple mixtures [[[1]](#endnote-1)]. Successful optimization requires a user with sufficient experience to choose candidate column chemistries that are likely to be successful. Even experienced users of the technology will require a significant amount of time to then find the best column geometries and instrument conditions for the separation. To circumvent labor intensive trial and error optimizations, computer modeling of retention behavior of the compounds could help to simulate the optimization process [[[2]](#endnote-2)]. Moreover, accurately predicted retention times provide invaluable qualitative information when used in conjunction with mass spectrometry to confirm a compound’s identity [[[3]](#endnote-3),[[4]](#endnote-4),[[5]](#endnote-5)]. As well such a system would be particularly useful in distinguishing structural isomers which may have near-identical EI mass spectra.

A range of empirical and semi-empirical tools have been developed for the prediction of retention behavior of different classes of compounds under various chromatographic conditions. Many of these predictive models fall into the category of quantitative structure-retention relationships (QSRR) which derive relationships between chromatographic parameters and molecular structure properties (descriptors) of the analytes [[[6]](#endnote-6)]. Typically QSRR approaches are applied to either Kovats’ retention indices or linear temperature-programmed retention indices in contemporary GC practice [[[7]](#endnote-7)]. Various successful QSRR models have been applied to predict the retention indices of different classes of compounds [[[8]](#endnote-8), [[9]](#endnote-9), [[10]](#endnote-10), [[11]](#endnote-11), [[12]](#endnote-12)]. However, the collected retention index database poses a problem, in that there are significant differences in reported values for a single compound. For example, in the NISTMS 2008 database there are 191 values of retention index for Benzene on 100% dimethyl polysiloxane columns with maximum and minimum values of 702 and 630 units, respectively. These distributions arise from several factors including differences in operating conditions such as temperature or temperature program (which can be potentially corrected) [[[13]](#endnote-13)], identification error, measurement or instrumentation error, and concentration ratio of target analytes and the reference compounds [[[14]](#endnote-14)]. Furthermore, procedures to estimate retention indices for multidimensional chromatography are technologically challenging [[[15]](#endnote-15)] and an appropriate set of reference compounds for the second-dimension retention index has not been established.

An alternate route to the prediction of retention times is through the modelling of the thermodynamics of the separation. There are several ways in which the thermodynamic data can be obtained [[[16]](#endnote-16), [[17]](#endnote-17), [[18]](#endnote-18), [[19]](#endnote-19), [[20]](#endnote-20), [[21]](#endnote-21) ] Recently, we have introduced an approach that relies data from multiple temperature-programmed separations with different ramp rates to obtain the raw data from which thermodynamic parameters are obtained [[[22]](#endnote-22)]. This allows for the simultaneous collection of data to obtain thermodynamic parameters for as many compounds as can be resolved and identified in the series of chromatograms.

Once thermodynamic parameters of enthalpy (∆H), entropy (∆S) and adiabatic molar heat capacity (ΔCp) have been obtained, the partition coefficient, and thus retention factor of the analyte on a column with known phase ratio may be calculated. This in turn permits the retention time of the molecule to be calculated using, for example, a model that iteratively calculates the distance the molecule travels in a finite, short period of time, given the instantaneous conditions of temperature, pressure, column geometry, etc… at the position of the band [2,16,7].

While obtaining thermodynamic data for hundreds of compounds in a matter of days is now possible, there are a limited number of standard molecules available. It would also be useful to be able to predict thermodynamic parameters for molecules that are not contained in the library. This would expand the library and increase the potential utility of thermodynamic data, especially in studies of complex mixtures of isomeric species. To this end, we present a study wherein a modest library of thermodynamic data spanning a range of alkanes, alcohols and alkyl halides has been developed. Additionally, the potential of QSRR modeling of thermodynamic data is investigated for these compounds. A series of linear models were tested and the results were evaluated using Monte-Carlo and leave-one-out cross validation.

**2. Materials and methods**

2.1 Chemicals

The list of chemicals used in this study is provided in Table 1S (Supplemental materials). The analytical grade standard solutions were obtained from the Chemical Exchange, (Environment, Health and Safety, University of Alberta) and originated from a variety of vendors including Sigma-Aldrich (Oakville, ON), Fisher Scientific (Ottawa, ON), Matheson Coleman & Bell (Cincinnati, OH), and Alfa-Aesar (Ward Hill, MA). In order to verify the purity and identity of all compounds, a solution of 100 μg/mL of each compound was prepared in pentane or dichloromethane and then analyzed by gas chromatography mass spectrometry (GC-MS). For compounds that were not conclusively identified by GC-MS, additional analysis was carried out using 1H NMR spectroscopy. Finally, 12 mixtures of the test molecules were prepared at concentrations between 250 and 600 μg/mL using careful selection of the compounds to avoid coelutions. ACS grade pentane and dichloromethane (Sigma-Aldrich) served as the solvents for all mixtures.

2.2 Instrumental

All experiments to generate thermodynamic data and test the models were conducted using a 7890A gas chromatograph (Agilent Technologies, Mississauga, ON) equipped with a 7683 Series auto sampler, a split/splitless injector, and flame ionization detector. Sample injection volume was 1 μL in split mode with a split ratio of 100:1 and an inlet temperature of 280 °C. All experiments were carried out on a 5 % phenyl substituted polydimethylsiloxane column (SLB5-ms) of dimensions 30 m × 0.25 mm; 0.25 μm (Supleco, Oakville, ON). The separations were initiated at 30 °C, with temperature-programmed ramp rates of 3, 5, 8, 10, 12, 16, and 20 °C·min-1to a final temperature of 250 °C. Hydrogen was used as the carrier gas (H2 99.999%, Praxair, Edmonton, AB) at a flow rate of 1.05 mL·min-1. The flame ionization detector was maintained at 250 °C with a data sampling rate of 100 Hz.

GC-MS analyses were conducted using a 7890A GC coupled to an Agilent 5975C MS (Agilent Technologies, Mississauga, ON) equipped with a 7683 Series auto sampler. The column was the same phase as used in the GC-FID experiments and helium was used as the carrier gas. The transfer line temperature was held at 270 °C. The sample injection volume was 1 μL, using a 200:1 split ratio. Electron impact ionization (70 eV) was used with a quadrupole mass analyzer in full scan mode (15-400 amu). NMR spectra were acquired in DMSO at 25°C on a Varian (Mississauga, ON) 400 MHz spectrometer.

2.3 Modeling procedure

In GC, the partition coefficient of an analyte is related to the enthalpy and entropy of the analyte at some reference temperature, Δ*H*(*T0*) and Δ*S*(*T0*), respectively, as well as the change in its adiabatic molar heat capacity, Δ*CP* by Equations (1) and (2) [17].

 (1)

 (2)

where *T0* is a reference temperature (typically 90 °C in our research) and *R* is the universal gas constant.

Once the chromatographic conditions (temperature programs, inlet and outlet pressures, column dimensions) are precisely known, the distance traveled by the analyte can be estimated by combining the estimated partition coefficient with the time summation model introduced by Snijders et al. [7]. In this work, thermodynamic parameters for the molecules under study were obtained using an approach described previously [22].

The collected thermodynamic parameters were then used to construct a series of QSRR models. A separate QSRR model was generated for each class of compounds, specifically: alkanes, alcohols, and alkyl halides. The three-dimensional structures of the molecules were optimized using Hamiltonian AM1, implemented in HyperChem v.6.0 (www.hyper.com). Molecular descriptors were calculated using Dragon v.03 (http://www.disat.unimib.it/chm). The calculated descriptors consisted of constitutional, topological, electronic, thermodynamic, and geometric descriptors. After removing constant, zero and highly correlated (correlation coefficient >0.9) descriptors, a total of 118, 195 and 414 descriptors remained for alkanes, alcohols, and alkyl halides, respectively.

QSRR models were coded in-house with the MATLAB environment (version 8.1.0.604 R2013a). The calculations were implemented on a personal computer with an AMD Athlon 64 ×2 Dual core 4800, 2.5 GHz processor with 6 GB RAM and running Windows 7 Enterprise operating system.

**3. Results and discussion**

3.1 Thermodynamic modeling

Five data points were collected for each analyte to obtain an accurate estimation of its thermodynamic parameters from temperature-programmed GC data [22]. In order to obtain sufficient data to estimate the thermodynamic parameters from the non-linear optimization and validate the estimations, the 12 mixtures were injected at seven different temperature ramp rates (3, 5, 8, 10, 12, 16, 20 °C⋅min-1). Evaluation of the model was carried out via internal and external validation. To begin, the data points from 8 and 16 °C⋅min-1 were omitted from the whole data set for each analyte. These two data points were reserved as the external sets to evaluate the performance of the model. The thermodynamic parameters of the analytes were calculated using the remaining 5 ramp rates in a leave-one out (LOO) regime. In this procedure, each ramp was consecutively excluded from the data and the thermodynamic parameters were calculated from the remaining data points. The determined thermodynamic parameters were used to predict the retention times of the left out ramp. Table 1 lists the thermodynamic parameters and the LOO predicted retention times of three selected molecules. The error plots of the LOO procedure for all compounds are depicted in Fig. 1. Statistical parameters of the LOO models are presented in Table 2. Root mean square error values of the models were all lower than 0.5 s with the largest error across all analytes and the temperature ramps being 1.46 s which shows good agreement between the experimental and the predicted retention times.

The best way to evaluate robustness of a model is to test it using an external set of data. Thus, the average values for each thermodynamic parameter (of the five estimations) were used to predict the retention time of the two left-out temperature ramps (8 and 16 °C·min-1). The performance of the model using the external set is also shown in Table 2. The residual plots of the external data (Fig. 2) show a random distribution about the zero line which indicates no dominant feature in the residuals. In other words, the new procedure for the calculation of thermodynamic parameters using temperature programming could be properly used to predict retention times of the analytes under these conditions. The experimental and predicted retention times of all compounds for the two temperature ramps of 8 and 16 °C·min-1 are given in Table 1S.

3.2 QSRR modeling

Although temperature-programmed thermodynamic modeling is quite fast and accurate, it is practically impossible to analyze all compounds even if looking only at a single family of molecules (e.g. alkanes). An efficient manner in which to obtain a library of thermodynamic parameters for a wide range of molecules would be to expand the available data using QSRR modeling. Ideally, the relationship between the chemical structure and the thermodynamic parameters is describable in reliable quantitative terms. In order to obtain statistically significant relationships, one requires a relatively large series of thermodynamic information [[[23]](#endnote-23)]. Such a library of experimental data is only now practical to obtain.

In order to have robust QSRR models, the data were split into three categories: alkanes, alcohols, and alkyl halides with 44, 52, and 60 analytes respectively. Before performing any QSRR modeling, the dataset for each category was split into training and test sets using a SPXY algorithm [[[24]](#endnote-24)]. In this context, 75% of the data were used as the training set and the remaining 25% as the test set. Multiple linear regression (MLR), and partial least squares regression (PLS) were used to estimate the thermodynamic parameters of the analytes. Simplicity and ease of use were the main reasons that linear models were tested for predictions here. As the PLS models gave better statistical results, the MLR results will not be discussed.

 Partition coefficients of the analytes in the training set were calculated at temperatures from 30 °C to 250 °C in 5 °C increments based on the measured thermodynamic parameters. These partition coefficients were used as the dependent variables of the QSRR models. Finally the predicted partition coefficients, which were derived from the QSRR models, were used to predict the thermodynamic parameters of new molecules.

3.3

* 1. QSRR modeling of alkanes

To develop a model using PLS, Monte-Carlo cross validation (MCCV) was performed on the training data at 90 °C and was repeated 1000 times. The RMSE values of the validation set were averaged across all the models to pick the best number of latent variables. According to Fig. 3 a model with five latent variables was chosen as the best model. Therefore, a PLS model with 5 latent variables was employed at each temperature and the estimated PLS coefficients were used to predict the partition coefficients. Once the partition coefficients were predicted, they were used for the estimation of the thermodynamic parameters followed by the prediction of retention times. Fig. 4 shows the Pareto plot and also the relative percent errors of the predicted retention times of the alkanes at two temperature ramps (3 and 20 °C·min-1). The results show that the QSRR methodology is able to successfully predict the thermodynamic parameters. The detailed statistical parameters of the model are presented in Table 3. Although the error values are larger than those from direct thermodynamic modeling (section 3.1), the error is still small enough to estimate precisely the retention order and the retention region of the compounds. As shown in Fig. 4 and Table 3, the percent errors of the predicted retention time on a given temperature ramp decreases with retention time. In the other words, the molecules with short retention time show higher relative prediction errors than the molecules with longer retention times. Additionally, an increase in temperature ramp rate leads to a decrease in the prediction error. These trends could possibly be due to interference of an adsorption process on the retention mechanism which has more effect at lower temperatures [[[25]](#endnote-25)].

3.4 QSRR modeling of alcohols and alkyl halides

The same procedure as the QSRR modeling of alkanes was carried out to build QSRR models for alcohols and alkyl halides. The MCCV method gave 9 and 11 latent variables for alcohols and alkyl halides, respectively. The statistical parameters of the models are given in Table 3. A comparison between results shows a decrease in prediction error with increasing temperature ramp rates for both series of the compounds. Due to presence of functional groups in the molecules, the QSRR models for alcohols and alkyl halides are not as good as the alkanes. Pareto plots and the percent error for two selected temperature ramps of the models for alcohols and alkyl halides are shown in Figs 5 and 6, respectively.

3.5 Important descriptors

A PLS method needs some sort of criterion to identify the most influential variables (descriptors) on the model. PLS loading weights, magnitude of the PLS regression coefficients and variable importance on PLS projections (VIP) are the three most commonly employed criteria for ordering the variables with respect to their importance [[[26]](#endnote-26), [[27]](#endnote-27), [[28]](#endnote-28)] In this study, VIP scores were calculated using the Eq. 3 to find the most predictive descriptors [29].

where, *p* is the number of variables, *M* is the number of latent variables, *wm,i*is the PLS weight of *i-*th variable for the *m*-thlatent variable and SS(bmtm) is the explained variance of y by the *m*-th latent variable. Normally, a threshold of one is chosen as the criteria for variable importance. *VIP* plots of the three PLS models for alkanes, alcohols, and alkyl halides are shown in Figs 1S, 2S and 3S, respectively.

The most important descriptor for alkanes was determined to be X1sol. This descriptor defines the solvation entropy and describes the dispersion interaction [[[29]](#endnote-29)]. This is reassuring, given that the dominant forces on 5% phenyl phases and only significant forces for alkanes in GC are dispersive forces. The quadrupole moment of the molecules weighted by atomic Sanderson electronegativity (Qe) and molecular masses (Qm), have the most significance on the retention behavior of alcohols and alkyl halides, respectively. These parameters quantify the extent to which the molecular charge distribution is deviated from sphericity. In addition to the charge distribution, the ratio of the π and lone-pair electrons over the count of the sigma bonds (E-state index) also has a high contribution towards the retention mechanism of alcohols. This index is a measure of electric accessibility and molecular polarity. Moreover, the branching index of the molecules (SPI) and dispersion interaction (X1sol) are the next two important descriptors which describe the retention behavior of alcohols. Length to breath ratio (L/B, a shape parameter) and Zagreb index (a molecular branching index) are two other important parameters for the retention of alkyl halides.

**4. Conclusions**

The approach of modeling of thermodynamic parameters based on temperature-programmed retention data has been evaluated more thoroughly than before using a suite of analytes comprising alkanes, alcohols, and alkyl halides. As long as the chromatographic peaks of the analytes could be tracked through the full series of temperature-programmed separations, the thermodynamic parameters of the analytes could be easily estimated.

Three QSRR models have been successfully built for alkanes, alcohols, and alkyl halides to demonstrate the possibility of *in silico* extending the thermodynamic library for the prediction of molecules that have not been observed previously.

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**References**

Table 1. Thermodynamic parameters of three selected molecules with their predicted retention times.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Name | Temperature ramp (°C⋅min-1) | Estimated ΔH (To)(kJ·mol-1) | EstimatedΔS(To)(J·K-1·mol-1) | EstimatedΔCp (J·K-1·mol-1) | tR(Exp)(min) | tR(Pred)(min) | Error(s) |
| 1,2,3-tribromo-2-methyl propane | 3 | -46.92 | -66.86 | 66.19 | 24.154 | 24.163 | -0.5 |
| 5 | -46.84 | -66.64 | 65.93 | 16.991 | 16.990 | 0.1 |
| 10 | -46.85 | -66.67 | 66.32 | 10.500 | 10.500 | 0.0 |
| 12 | -46.85 | -66.67 | 66.45 | 9.257 | 9.257 | 0.0 |
| 20 | -46.84 | -66.64 | 65.93 | 6.537 | 6.538 | -0.1 |
| 4-heptanol | 3 | -39.14 | -64.04 | 82.31 | 9.793 | 9.797 | -0.2 |
| 5 | -39.11 | -63.96 | 81.56 | 7.808 | 7.807 | 0.1 |
| 10 | -39.12 | -63.98 | 80.89 | 5.580 | 5.582 | -0.1 |
| 12 | -39.12 | -63.98 | 81.16 | 5.094 | 5.095 | 0.0 |
| 20 | -39.13 | -64.01 | 80.90 | 3.946 | 3.947 | 0.0 |
| 4-methyl nonane | 3 | -41.96 | -67.64 | 61.94 | 12.771 | 12.780 | -0.5 |
| 5 | -41.94 | -67.58 | 60.43 | 9.765 | 9.762 | 0.2 |
| 10 | -42.20 | -68.30 | 46.93 | 6.642 | 6.642 | 0.0 |
| 12 | -42.20 | -68.30 | 46.93 | 5.991 | 5.992 | 0.0 |
| 20 | -42.20 | -68.30 | 46.93 | 4.499 | 4.498 | 0.0 |

Table 2. Statistical parameters of thermodynamic models at different temperature ramps.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Temperature Ramps** | **3 LOO (°C⋅min-1)** | **5LOO (°C⋅min-1)** | **8Ext (°C⋅min-1)** | **10 LOO (°C⋅min-1)** | **12 LOO (°C⋅min-1)** | **16 Ext (°C⋅min-1)** | **20 LOO (°C⋅min-1)** |
| **R2** | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| **RMSE (s)** | 0.390 | 0.175 | 0.075 | 0.074 | 0.057 | 0.065 | 0.124 |
| **Errormax (s)** | 1.30 | 0.59 | 0.27 | 0.39 | 0.16 | 0.19 | 0.29 |
| **Errormin (s)** | -1.46 | -0.68 | -0.15 | -0.18 | -0.14 | -0.25 | -0.57 |

LOO: Refers to leave one out cross validation, Ext: Refers to external set validation.

Table 3. Statistical parameters of PLS models developed based on the thermodynamic parameters.

|  |  |  |
| --- | --- | --- |
|  |  | **Temperature ramps (°C⋅min-1)** |
|  |  | **3** | **5** | **8** | **10** | **12** | **16** | **20** |
| **Alkanes** | R2tr | 0.999 | 0.999 | 0.999 | 0.999 | 0.999 | 0.999 | 0.999 |
| R2te | 0.998 | 0.998 | 0.998 | 0.998 | 0.998 | 0.998 | 0.998 |
| RRMSEtr% | 1.73 | 1.56 | 1.40 | 1.31 | 1.24 | 1.14 | 1.05 |
| RRMSEte% | 2.49 | 2.14 | 1.83 | 1.69 | 1.58 | 1.42 | 1.30 |
| **Alcohols** | R2tr | 0.999 | 0.999 | 0.999 | 0.999 | 0.999 | 0.999 | 0.999 |
| R2te | 0.996 | 0.995 | 0.994 | 0.994 | 0.993 | 0.992 | 0.991 |
| RRMSEtr% | 1.70 | 1.57 | 1.56 | 1.41 | 1.36 | 1.28 | 1.20 |
| RRMSEte% | 2.33 | 2.36 | 2.40 | 2.41 | 2.43 | 2.42 | 2.42 |
| **Alkyl Halides** | R2tr | 0.998 | 0.998 | 0.998 | 0.998 | 0.998 | 0.998 | 0.998 |
| R2te | 0.997 | 0.997 | 0.997 | 0.997 | 0.997 | 0.997 | 0.997 |
| RRMSEtr% | 2.31 | 2.08 | 1.88 | 1.78 | 1.70 | 1.58 | 1.48 |
| RRMSEte% | 3.35 | 2.99 | 2.65 | 2.46 | 2.32 | 2.08 | 1.91 |

tr: Refers to training set, te: Refers to test set.

Figure Captions

Fig. 1. Residual plots of LOO predicted obtained from direct thermodynamic modeling.



Fig. 2. Residual plots of external set predicted from direct thermodynamic modeling.



Fig. 3. RMSE values of calibration and validation sets for alkanes using PLS models. Open circles: RMSE values of the training set, star symbols: RMSE values of the validation set



Fig. 4. Pareto plots and error bar plots of two selected temperature ramps obtained from PLS modeling on alkanes dataset.



Fig. 5. Pareto plots and error bar plots of two selected temperature ramps obtained from PLS modeling on alcohols dataset.



Fig. 6. Pareto plots and error bar plots of two selected temperature ramps obtained from PLS modeling on alkylhalides dataset.



**Supplemental Data**

**Quantitative Structure-Retention Relationship Modeling of Gas Chromatographic Retention Times Based on Thermodynamic Data**

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Table 1S: Name of the compounds along with their experimental and predicted retention times at two different temperature ramps.

|  |  | Temperature ramp 8 | Temperature ramp 16 |
| --- | --- | --- | --- |
| **#** | **Name**  | **tR(Exp.)****(min)** | **tR(Pred.)****(min)** | **Error****(s)** | **tR(Exp.)****(min)** | **tR(Pred.)****(min)** | **Error****(s)** |
| 1 | 2-Methyl 2-Butanol | 2.654 | 2.653 | 0.01 | 2.352 | 2.348 | 0.19 |
| 2 | 1,2-diChloroethane | 2.722 | 2.722 | 0.05 | 2.406 | 2.405 | 0.03 |
| 3 | 2-Methyl Hexane | 2.822 | 2.820 | 0.09 | 2.465 | 2.465 | 0.00 |
| 4 | 1-Chloro-2,2-diMethyl Propane  | 2.836 | 2.835 | 0.06 | 2.481 | 2.482 | -0.04 |
| 5 | 2-Chloro-2-methyl Butane | 2.844 | 2.843 | 0.04 | 2.486 | 2.487 | -0.04 |
| 6 | 2,2-diMethyl 1-propanol | 2.911 | 2.912 | -0.04 | 2.517 | 2.518 | -0.08 |
| 7 | 3-Methyl Hexane | 2.915 | 2.915 | 0.00 | 2.527 | 2.528 | -0.08 |
| 8 | 2-Iodopropane  | 2.921 | 2.920 | 0.06 | 2.542 | 2.542 | 0.02 |
| 9 | 3-Ethyl Pentane | 3.026 | 3.027 | -0.04 | 2.599 | 2.600 | -0.06 |
| 10 | 2,2,4-triMethyl Pentane | 3.050 | 3.052 | -0.07 | 2.619 | 2.620 | -0.06 |
| 11 | Heptane | 3.172 | 3.172 | -0.01 | 2.687 | 2.688 | -0.08 |
| 12 | Trans 3-pentene-2-ol | 3.218 | 3.220 | -0.09 | 2.706 | 2.705 | 0.09 |
| 13 | 3-Pentanol | 3.228 | 3.228 | 0.01 | 2.716 | 2.715 | 0.06 |
| 14 | 2-Methyl 4-Pentene 2-ol | 3.365 | 3.365 | 0.00 | 2.802 | 2.803 | -0.08 |
| 15 | 1-Chloro-3-Methyl Butane | 3.411 | 3.412 | -0.04 | 2.842 | 2.843 | -0.08 |
| 16 | 2,2-di Methyl Hexane | 3.421 | 3.420 | 0.06 | 2.843 | 2.845 | -0.12 |
| 17 | 4-Pentene 2-ol | 3.439 | 3.437 | 0.14 | 2.870 | 2.870 | 0.00 |
| 18 | 2,5-diMethyl Hexane | 3.548 | 3.547 | 0.08 | 2.919 | 2.920 | -0.06 |
| 19 | 1-Bromobutane | 3.570 | 3.570 | 0.00 | 2.943 | 2.942 | 0.08 |
| 20 | 3-Methyl 1-Butanol | 3.679 | 3.675 | 0.24 | 2.981 | 2.982 | -0.04 |
| 21 | 2-Methyl-1-Butanol | 3.722 | 3.723 | -0.08 | 3.012 | 3.013 | -0.08 |
| 22 | 3,3-diMethyl -2-Butanol | 3.728 | 3.727 | 0.08 | 3.027 | 3.027 | 0.02 |
| 23 | 3-Chloropropanol | 3.744 | 3.743 | 0.04 | 3.021 | 3.022 | -0.04 |
| 24 | 2-Bromo 2-Methyl Butane | 3.773 | 3.773 | -0.02 | 3.072 | 3.072 | -0.01 |
| 25 | 3-Ethyl 2-Methyl Pentane | 3.987 | 3.987 | 0.02 | 3.186 | 3.187 | -0.04 |
| 26 | 1-Pentanol | 4.127 | 4.128 | -0.08 | 3.244 | 3.243 | 0.01 |
| 27 | 2,2,4,4-tetraMethyl Pentane | 4.151 | 4.150 | 0.06 | 3.288 | 3.288 | -0.05 |
| 28 | 3-Methyl Heptane | 4.157 | 4.155 | 0.12 | 3.277 | 3.278 | -0.05 |
| 29 | 5-Hexene-3-ol | 4.188 | 4.188 | -0.02 | 3.294 | 3.293 | 0.04 |
| 30 | 1-Bromo-2-propanol | 4.200 | 4.200 | 0.00 | 3.298 | 3.298 | -0.02 |
| 31 | 2-Methyl -3-Pentanol | 4.240 | 4.238 | 0.10 | 3.337 | 3.338 | -0.08 |
| 32 | 2,2-diChloroethanol | 4.284 | 4.283 | 0.04 | 3.351 | 3.352 | -0.04 |
| 33 | 1-Iodopropane | 4.365 | 4.363 | 0.10 | 3.396 | 3.397 | -0.04 |
| 34 | Butane 2,3-diol | 4.380 | 4.380 | 0.00 | 3.378 | 3.378 | -0.02 |
| 35 | 1-Iodo-2-Methyl Propane | 4.397 | 4.397 | 0.02 | 3.439 | 3.440 | -0.06 |
| 36 | 2,2,4-triMethyl Hexane | 4.422 | 4.422 | 0.02 | 3.440 | 3.440 | 0.00 |
| 37 | 1-Bromo-3-methyl Butane | 4.518 | 4.517 | 0.08 | 3.499 | 3.500 | -0.06 |
| 38 | 3-Hexanol | 4.570 | 4.568 | 0.10 | 3.503 | 3.503 | -0.02 |
| 39 | 2-Hexanol | 4.639 | 4.638 | 0.04 | 3.538 | 3.537 | 0.08 |
| 40 | 2,2-diMethyl Heptane | 4.889 | 4.890 | -0.03 | 3.696 | 3.697 | -0.04 |
| 41 | 3-Bromo-1-Propanol | 4.908 | 4.908 | -0.02 | 3.690 | 3.690 | 0.00 |
| 42 | 2,4-diMethyl Heptane | 4.940 | 4.940 | 0.03 | 3.722 | 3.722 | -0.01 |
| 43 | 1-Bromopentane | 5.171 | 5.168 | 0.16 | 3.862 | 3.865 | -0.15 |
| 44 | 3,5-diMethyl Heptane | 5.178 | 5.178 | 0.01 | 3.855 | 3.855 | 0.00 |
| 45 | 3,3-diMethyl Heptane | 5.224 | 5.222 | 0.14 | 3.882 | 3.887 | -0.25 |
| 46 | 4-Methyl Pentanol | 5.258 | 5.257 | 0.08 | 3.876 | 3.877 | -0.01 |
| 47 | 3-Methyl -1-Pentanol | 5.421 | 5.420 | 0.06 | 3.968 | 3.970 | -0.12 |
| 48 | 2,3-diMethyl Heptane | 5.557 | 5.555 | 0.12 | 4.061 | 4.062 | -0.04 |
| 49 | 3,4-diMethyl Heptane | 5.602 | 5.602 | 0.02 | 4.086 | 4.087 | -0.04 |
| 50 | 4-Ethyl Heptane | 5.624 | 5.622 | 0.14 | 4.094 | 4.093 | 0.04 |
| 51 | 1,2-diBromopropane | 5.660 | 5.658 | 0.10 | 4.151 | 4.152 | -0.04 |
| 52 | 2-Bromo-3-Methyl Pentane | 5.696 | 5.693 | 0.16 | 4.163 | 4.165 | -0.12 |
| 53 | 2-Methyl Octane | 5.718 | 5.718 | -0.02 | 4.141 | 4.142 | -0.04 |
| 54 | Trans 2-Hexene 1-ol | 5.773 | 5.772 | 0.08 | 4.158 | 4.158 | -0.02 |
| 55 | 1-Hexanol | 5.835 | 5.835 | 0.00 | 4.189 | 4.190 | -0.06 |
| 56 | 3,3-diEthyl Pentane | 5.972 | 5.973 | -0.11 | 4.312 | 4.312 | 0.02 |
| 57 | 1-Chlorohexane | 6.045 | 6.045 | 0.00 | 4.311 | 4.312 | -0.04 |
| 58 | 4-Heptanol | 6.232 | 6.232 | 0.05 | 4.410 | 4.410 | 0.00 |
| 59 | 1,3-diChloro-2-propanol | 6.385 | 6.383 | 0.10 | 4.517 | 4.518 | -0.08 |
| 60 | 1-Bromo-4-Methyl Pentane | 6.404 | 6.400 | 0.27 | 4.529 | 4.532 | -0.16 |
| 61 | Pentane 1,2-diol | 6.563 | 6.562 | 0.08 | 4.587 | 4.587 | 0.02 |
| 62 | 2,2-diMethyl Octane | 6.694 | 6.692 | 0.11 | 4.661 | 4.662 | -0.04 |
| 63 | 4,4-diMethyl Octane | 6.720 | 6.720 | 0.03 | 4.682 | 4.682 | 0.02 |
| 64 | 2,2,6,6-tetraMethyl Heptane | 6.738 | 6.738 | -0.02 | 4.688 | 4.688 | -0.05 |
| 65 | 3,5-diMethyl Octane (RR) | 6.779 | 6.778 | 0.04 | 4.708 | 4.710 | -0.12 |
| 66 | 3,5-diMethyl Octane (RS) | 6.819 | 6.820 | -0.06 | 4.728 | 4.728 | -0.02 |
| 67 | Methylene Iodide | 6.826 | 6.827 | -0.04 | 4.792 | 4.792 | 0.02 |
| 69 | 2,3-diBromobutane (R,R) | 6.898 | 6.897 | 0.08 | 4.821 | 4.822 | -0.04 |
| 70 | 6-Bromo-1-hexene | 6.902 | 6.900 | 0.12 | 4.790 | 4.790 | 0.00 |
| 71 | 1-Bromo-3-Chloro-2-Methyl propane | 7.000 | 7.000 | 0.00 | 4.856 | 4.855 | 0.06 |
| 72 | 2,6-diMethyl Octane | 7.006 | 7.005 | 0.06 | 4.825 | 4.823 | 0.10 |
| 73 | 3,3-diMethyl Octane | 7.036 | 7.035 | 0.06 | 4.849 | 4.850 | -0.06 |
| 74 | 3,4-diEthyl Hexane | 7.075 | 7.075 | 0.00 | 4.878 | 4.880 | -0.12 |
| 75 | 1-Bromohexane | 7.077 | 7.075 | 0.12 | 4.884 | 4.883 | 0.04 |
| 76 | 3,6-diMethyl Octane | 7.108 | 7.107 | 0.05 | 4.883 | 4.883 | -0.02 |
| 77 | 3-Chloro Propane-1,2-diol | 7.136 | 7.137 | -0.04 | 4.899 | 4.898 | 0.07 |
| 78 | 4-Propyl Heptane | 7.189 | 7.188 | 0.07 | 4.918 | 4.918 | -0.02 |
| 79 | 2,3-diBromobutane(R,S) | 7.219 | 7.218 | 0.04 | 4.988 | 4.987 | 0.08 |
| 80 | 4-Methyl Hexanol | 7.249 | 7.250 | -0.03 | 4.939 | 4.938 | 0.04 |
| 81 | 1,3-diBromopropane | 7.346 | 7.345 | 0.06 | 5.046 | 5.047 | -0.07 |
| 82 | 2-Butene 1,4-diol | 7.383 | 7.382 | 0.08 | 4.991 | 4.988 | 0.16 |
| 83 | 5-Methyl Nonane | 7.487 | 7.487 | 0.02 | 5.072 | 5.072 | -0.01 |
| 84 | 4-Methyl Nonane | 7.530 | 7.530 | 0.00 | 5.095 | 5.095 | 0.00 |
| 85 | 1,2-diBromobutane | 7.558 | 7.558 | -0.02 | 5.163 | 5.165 | -0.12 |
| 86 | 3-Methyl Nonane | 7.722 | 7.722 | 0.02 | 5.195 | 5.195 | 0.00 |
| 87 | 1-Heptanol | 7.729 | 7.728 | 0.04 | 5.186 | 5.187 | -0.04 |
| 88 | 1-Octene 3-ol | 7.906 | 7.907 | -0.04 | 5.285 | 5.285 | 0.00 |
| 89 | 3,3,4,4-tetraMethyl Hexane | 7.926 | 7.927 | -0.04 | 5.344 | 5.343 | 0.04 |
| 90 | 3,3,3-triChloro-2-Methyl-2-Propanol | 7.937 | 7.935 | 0.12 | 5.348 | 5.347 | 0.08 |
| 91 | 1,3-diBromobutane | 8.141 | 8.140 | 0.06 | 5.463 | 5.463 | -0.02 |
| 92 | Decane | 8.282 | 8.282 | 0.05 | 5.485 | 5.485 | 0.00 |
| 93 | 2-Octanol | 8.322 | 8.322 | 0.02 | 5.493 | 5.493 | -0.02 |
| 94 | 1,5-diChloropentane | 8.786 | 8.783 | 0.13 | 5.769 | 5.770 | -0.06 |
| 95 | 1,2-diBromo-1,1,diChloroethane | 8.937 | 8.937 | 0.02 | 5.887 | 5.888 | -0.08 |
| 96 | 1-Bromoheptane | 9.058 | 9.058 | -0.02 | 5.906 | 5.907 | -0.01 |
| 97 | 3,5,5-triMethyl 1-Hexanol | 9.192 | 9.192 | 0.02 | 5.957 | 5.957 | 0.02 |
| 98 | 2-Ethyl 2-Methyl Propane 1,3-diol | 9.319 | 9.320 | -0.06 | 6.014 | 6.013 | 0.04 |
| 99 | 1-Chlorooctane | 9.465 | 9.465 | 0.00 | 6.104 | 6.105 | -0.06 |
| 100 | 1-Octanol | 9.637 | 9.637 | 0.02 | 6.167 | 6.167 | 0.02 |
| 101 | 1,4-diBromobutane | 9.763 | 9.763 | -0.02 | 6.298 | 6.298 | -0.02 |
| 102 | 5-Nonanol | 9.981 | 9.982 | -0.04 | 6.349 | 6.348 | 0.04 |
| 103 | 4-Nonanol | 9.997 | 9.997 | 0.02 | 6.357 | 6.357 | 0.02 |
| 104 | 2,3-diBromo-1-propanol | 10.068 | 10.070 | -0.09 | 6.459 | 6.458 | 0.07 |
| 105 | 3-Nonanol | 10.132 | 10.132 | -0.01 | 6.430 | 6.428 | 0.07 |
| 106 | 2-Nonanol | 10.204 | 10.202 | 0.14 | 6.457 | 6.457 | 0.02 |
| 107 | 4-Methyl 4-Nonanol | 10.602 | 10.600 | 0.09 | 6.669 | 6.668 | 0.04 |
| 108 | 1,6-diChlorohexane | 10.763 | 10.763 | -0.02 | 6.782 | 6.780 | 0.12 |
| 109 | 1-Iodoheptane | 10.802 | 10.802 | 0.05 | 6.812 | 6.812 | -0.01 |
| 110 | 7-Methyl 1-Octanol | 10.841 | 10.842 | -0.04 | 6.783 | 6.783 | -0.02 |
| 111 | 6-Chloro-1-Hexanol | 10.877 | 10.877 | 0.02 | 6.817 | 6.818 | -0.08 |
| 112 | 2,2,2-triBromoethanol | 10.879 | 10.880 | -0.06 | 6.877 | 6.877 | 0.02 |
| 113 | Hexane 1,6-diol | 10.959 | 10.960 | -0.06 | 6.838 | 6.838 | -0.02 |
| 114 | 3-Methyl 5-Nonanol | 11.060 | 11.060 | 0.00 | 6.901 | 6.900 | 0.06 |
| 115 | 2-Methyl 5-Nonanol | 11.127 | 11.127 | 0.02 | 6.932 | 6.932 | 0.02 |
| 116 | 1,2-diBromohexane | 11.159 | 11.158 | 0.04 | 7.010 | 7.010 | 0.00 |
| 117 | Undecane | 11.172 | 11.170 | 0.10 | 7.453 | 7.453 | -0.02 |
| 118 | 2-Methyl 3-Nonanol | 11.353 | 11.353 | -0.02 | 7.051 | 7.050 | 0.06 |
| 119 | 1-Nonanol | 11.480 | 11.480 | 0.00 | 7.109 | 7.110 | -0.06 |
| 120 | 5-Decnol | 11.796 | 11.798 | -0.14 | 7.276 | 7.277 | -0.01 |
| 121 | 4-Decanol | 11.820 | 11.820 | -0.03 | 7.287 | 7.287 | 0.02 |
| 122 | 2-Bromononane | 11.853 | 11.852 | 0.08 | 7.328 | 7.330 | -0.09 |
| 123 | 1,5-diBromopentane | 11.946 | 11.947 | -0.01 | 7.406 | 7.407 | -0.01 |
| 124 | 1,2,3-triBromo-2-Methyl Propane | 12.257 | 12.257 | 0.02 | 7.601 | 7.602 | -0.04 |
| 125 | 3,7-diMethyl 6-Octene 1-ol | 12.450 | 12.448 | 0.10 | 7.605 | 7.605 | 0.00 |
| 126 | 8-Methyl 1-Nonanol | 12.612 | 12.612 | 0.02 | 7.686 | 7.683 | 0.16 |
| 127 | 1-Bromononane | 12.821 | 12.820 | 0.06 | 7.821 | 7.822 | -0.04 |
| 128 | Geraniol | 12.869 | 12.868 | 0.04 | 7.821 | 7.822 | -0.04 |
| 129 | Dodecane | 12.997 | 12.995 | 0.10 | 8.381 | 8.382 | -0.04 |
| 130 | 1,1,2,2-tetraBromoethane | 13.513 | 13.513 | -0.02 | 8.241 | 8.240 | 0.06 |
| 131 | 5-Undecanol | 13.515 | 13.513 | 0.10 | 8.143 | 8.142 | 0.08 |
| 132 | 1,6-diBromohexane | 13.814 | 13.815 | -0.06 | 8.357 | 8.357 | 0.02 |
| 133 | 1-Bromodecane | 14.559 | 14.558 | 0.04 | 8.701 | 8.702 | -0.04 |
| 134 | Tridecane | 14.729 | 14.728 | 0.06 | 9.260 | 9.258 | 0.08 |
| 135 | 1,1,1,2,3,3,3-Heptachloropropane | 15.089 | 15.092 | -0.13 | 9.054 | 9.053 | 0.01 |
| 136 | 1,5-diIodopentane | 15.418 | 15.420 | -0.12 | 9.202 | 9.200 | 0.15 |
| 137 | 1-Undecanol | 15.922 | 15.920 | 0.10 | 9.867 | 9.867 | 0.00 |
| 138 | Nonane 1,9-diol | 16.056 | 16.055 | 0.06 | 9.433 | 9.433 | -0.02 |
| 139 | 1-Iododecane | 16.104 | 16.103 | 0.01 | 9.496 | 9.495 | 0.06 |
| 140 | 1-Bromoundecane | 16.188 | 16.187 | 0.05 | 9.524 | 9.523 | 0.01 |
| 141 | Tetradecane | 16.261 | 16.262 | -0.02 | 10.043 | 10.043 | -0.02 |
| 142 | Pentadecane | 16.826 | 16.827 | -0.04 | 9.812 | 9.812 | 0.05 |
| 143 | 2-Bromododecane  | 16.891 | 16.892 | -0.04 | 9.876 | 9.878 | -0.14 |
| 144 | 1,8-diBromooctane | 17.216 | 17.217 | -0.04 | 10.077 | 10.077 | 0.02 |
| 145 | 1,2,3,4-tetraBromobutane | 17.448 | 17.447 | 0.08 | 10.242 | 10.242 | 0.02 |
| 146 | 1-Dodecanol | 17.498 | 17.498 | 0.00 | 10.665 | 10.667 | -0.06 |
| 147 | Hexadecane | 18.278 | 18.278 | -0.02 | 10.544 | 10.545 | -0.06 |
| 148 | 2-tetradecanol | 18.347 | 18.348 | -0.08 | 10.588 | 10.588 | -0.02 |
| 149 | 2-Bromotridecane | 18.391 | 18.390 | 0.06 | 10.636 | 10.635 | 0.06 |
| 150 | 1-Tridecanol | 19.023 | 19.018 | 0.26 | 11.439 | 11.440 | -0.08 |
| 151 | 1-Bromotridecane | 19.192 | 19.192 | 0.02 | 11.039 | 11.040 | -0.06 |
| 152 | Heptadecane | 19.654 | 19.655 | -0.06 | 11.241 | 11.242 | -0.04 |
| 153 | 2,6,10,14-tetraMethyl Pentadecane | 19.703 | 19.703 | -0.02 | 11.266 | 11.267 | -0.04 |
| 154 | 1-Tetradecanol | 20.427 | 20.425 | 0.10 | 12.150 | 12.148 | 0.08 |
| 155 | 1-Bromotetradecane | 20.590 | 20.592 | -0.07 | 11.756 | 11.755 | 0.03 |
| 156 | 1-Bromohexadecane | 23.142 | 23.145 | -0.15 | 13.030 | 13.030 | 0.03 |
| 157 | Eicosane | 23.395 | 23.395 | 0.00 | 13.131 | 13.130 | 0.06 |

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Fig. 1S. VIP plot of PLS models for alkanes.



Fig. 2S. VIP plot of PLS models for alcohols.



Fig. 3S. VIP plot of PLS models for alkylhalides.

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