

DEVELOPMENT OF CORRELATIONS FOR DESCRIBING SOLUTE TRANSFER INTO
ACYCLIC ALCOHOL SOLVENTS BASED ON THE ABRAHAM MODEL AND
FRAGMENT-SPECIFIC EQUATION COEFFICIENTS

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Abstract

Gas-to-alcohol partition coefficients have been compiled for 1880 different solute-alcohol combinations, which comprised 23 acyclic alcohols. These partition coefficients were converted into water-to-alcohol partition coefficients using the corresponding gas-to-water partition coefficients. Both sets of partition coefficients were analyzed using the Abraham solvation parameter model with fragment-specific equation coefficients. The derived equations correlated the experimental gas-to-alcohol and water-to-alcohol partition coefficient data to within 0.14 and 0.15 log units, respectively. The fragment-specific equation coefficients that have been calculated for the CH₃, CH₂, CH, C and OH fragment groups can be combined to yield expressions capable of predicting the partition coefficients of solutes in other anhydrous alcohol solvents.

KEY WORDS AND PHRASES: Partition Coefficients, Alcohol Solvents, Linear Free Energy
Correlations, Activity Coefficients, Solubilities, Henry's Constants

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1. Introduction

This study continues our application of the Abraham solvation parameter model to describe processes of chemical, biological and pharmaceutical importance. Past studies have shown that the basic model can provide reasonably accurate predictions for the solubility of crystalline and gaseous nonelectrolyte solutes dissolved in both water and organic solvents [1-5], for the partitioning of drug molecules between blood and select body organs [6-12], for the toxicity of organic compounds to various aquatic organisms [13-15], for the skin permeability of chemicals from aqueous solution [16], and for the minimum alveolar concentration for inhalation anesthesia to rats [17]. Each of the predicted properties involves either a direct or indirect solute partitioning processes.

The Abraham model [18, 19] relies on two linear free energy relationships, one for solute transfer between condensed phases

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

and for processes involving solute transfer from the gas phase to a condensed phase

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

The dependent variable in Eqns. 1 and 2, SP, is some property of a series of solutes in a fixed phase. For solubility predictions, Eqn. 1 assumes that the solute property is given by the logarithm of the ratio of molar solubilities of the solute in the organic solvent, C_S^{sat} , and in water, C_W^{sat} (i.e., $SP = \log [C_S^{\text{sat}}/C_W^{\text{sat}}]$). The solute property, SP, in Eqn. 2 is similarly calculated as the logarithm of the molar solubility in the organic solvent divided by the solute gas phase concentration (i.e., $SP = \log [C_S^{\text{sat}}/C_G]$), the latter value calculable from the solute vapor pressure

above the solid at the solution temperature. The computation methodology is described in detail elsewhere. [1-5]

The independent variables in Eqns. 1 and 2 are solute descriptors as follows: **E** and **S** refer to the excess molar refraction and dipolarity/polarity descriptors of the solute, respectively, **A** and **B** are measures of the solute hydrogen-bond acidity and hydrogen-bond basicity, **V** is the McGowan volume of the solute and **L** is the logarithm of the solute gas phase dimensionless Ostwald partition coefficient into hexadecane at 298 K. The regression coefficients and constants (c, e, s, a, b, v and l) are obtained by regression analysis of experimental data for a specific process (*i.e.*, a given partitioning process, for GLC or HPLC processes, a given stationary phase and mobile phase combination, *etc.*). In the case of partition coefficients, where two solvent phases are involved, the c, e, s, a, b, v and l coefficients represent differences in the solvent phase properties. For any fully characterized system/process (those with calculated values for the equation coefficients), further values of log P and log K can be estimated with known values for the solute descriptors.

The success of the Abraham model in predicting solute transfer properties for a wide range of practical applications prompted us to explore the feasibility of separating the equation coefficients by fragment contributions. In the first of these studies, Sprunger and coworkers [20-23] proposed a modified version of the Abraham model for correlating the gas-to-liquid solvent partition coefficient, K, and water-to-organic solvent partition coefficient, P, of solutes into room temperature ionic liquids (RTILs)

$$\log P = c_{\text{cation}} + c_{\text{anion}} + (e_{\text{cation}} + e_{\text{anion}}) \mathbf{E} + (s_{\text{cation}} + s_{\text{anion}}) \mathbf{S} + (a_{\text{cation}} + a_{\text{anion}}) \mathbf{A} + (b_{\text{cation}} + b_{\text{anion}}) \mathbf{B} + (v_{\text{cation}} + v_{\text{anion}}) \mathbf{V} \quad (3)$$

and

$$\log K = c_{\text{cation}} + c_{\text{anion}} + (e_{\text{cation}} + e_{\text{anion}}) \mathbf{E} + (s_{\text{cation}} + s_{\text{anion}}) \mathbf{S} + (a_{\text{cation}} + a_{\text{anion}}) \mathbf{A} + (b_{\text{cation}} + b_{\text{anion}}) \mathbf{B} + (l_{\text{cation}} + l_{\text{anion}}) \mathbf{L} \quad (4)$$

by rewriting each of the seven solvent equation coefficients as a summation of their respective cation and anion contributions. Very little loss in descriptive ability (less than 0.02 log units) resulted from splitting the equation coefficients into cation-specific and anion-specific values. The approach that Sprunger et al. developed allows one to utilize experimental data that otherwise would be unusable with the more traditional method of obtaining Abraham model correlations for a specific RTIL solvent. Moreover, once the cation-specific and anion-specific coefficients are calculated, new predictive equations can be written simply by summing the known values. The 11 cation-specific and 9-anion-specific equation coefficients that we now have reported, based on experimental chromatographic retention factor data and experimental partition coefficient data for 28 RTILs, can be combined to yield predictive Abraham model correlations for 99 RTILs.

The methodology that Sprunger and coworkers developed for RTILs can be extended to other solvent systems. In the present study we explore the possibility of developing a generic Abraham model correlation for alcohol solvents by splitting each equation coefficient into a fragment-specific contribution. The molecular fragments that are proposed include: a terminal CH^3 group, a CH_2 methylene group, a CH group, a tertiary C carbon atom, and the OH hydroxyl group. The proposed method is illustrated using 1879 experimental log P and 1880 experimental log K values for organic solutes and gases dissolved in anhydrous linear, secondary, tertiary and methyl-branched alcohols. For anhydrous alcohols, the log P values refer to a hypothetical

partition process as discussed in detail elsewhere [24-30]. Even though hypothetical, the derived log P correlations are still quite useful in that predicted log P values can be used to estimate the solute's infinite dilution activity coefficient or the solute's molar solubility in the anhydrous (dry) alcohol solvent. The solutes considered cover a wide range of chemical diversity and hydrogen-bonding characteristics. **For any given solute though there is about a 0.2 log unit difference in the log K value (or log P value) between the different alcohol solvents (except for ethylene glycol).**

2. Data Sets and Computation Methodology

The log P and log K values for solutes dissolved in methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-decanol, 2-propanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol and 3-methyl-1-butanol come from our recently published compilations [28-30]. Experimental log P and log K values for the remaining alcohols (2-pentanol, 2-methyl-1-pentanol, 2-methyl-2-butanol, 2-methyl-1-butanol, 4-methyl-2-pentanol, 3-pentanol, 2-ethyl-1-hexanol, 1-nonanol, and ethylene glycol) were calculated from published Raoult's law infinite dilution activity coefficient, γ_{solute}^{∞} , Henry's law constants, K_{Henry} , or solubilities for solutes dissolved in anhydrous alcohol solvents. In order to apply the Abraham model the infinite dilution activity coefficients and Henry's law constants needed to be converted to log K values through Eqns. 5 and 6

$$\log K = \log \left(\frac{RT}{\gamma_{solute}^{\infty} P_{solute}^o V_{solvent}} \right) \quad (5)$$

$$\log K = \log \left(\frac{RT}{K_{Henry} V_{solvent}} \right) \quad (6)$$

$$\log P = \log K - \log K_w \quad (7)$$

and to log P values for partition from water to the anhydrous alcohols through Eqn. 7. In equations 5 and 6, R is the universal gas constant, T is the system temperature, $P_{\text{solute}}^{\circ}$ is the vapor pressure of the solute at T, and V_{solvent} is the molar volume of the solvent. The calculation of log P requires knowledge of the solute's gas phase partition coefficient into water, K_w , which is available for most of the solutes being studied. The experimental log K and log P values at 298 K for all of the anhydrous alcohol solvents are listed in Tables S1 and S2 (Supporting Information), along with the respective literature references.

Our experimental databases also contain measured solubility data for several crystalline solutes dissolved in both the anhydrous alcohols and in water. The solubility data were taken largely from our previously published solubility studies. At the time that our solubility studies were performed we included solvents for which we planned to update and to derive correlation equations in the future. In the case of crystalline solutes, the partition coefficient between water and the anhydrous organic solvent is calculated as a solubility ratio

$$P = C_S/C_W \quad (8)$$

of the solute's molar solubilities in the organic solvent, C_S , and in water, C_W . Molar solubilities can also be used to calculate log K values, provided that the equilibrium vapor pressure of the solute above crystalline solute, $P_{\text{solute}}^{\circ}$, at 298 K is also available. $P_{\text{solute}}^{\circ}$ can be transformed into the gas phase concentration, C_G , and the gas-to-water and gas-to-organic solvent partitions, K_W and K, can be obtained through the following equations

$$K_W = C_W/C_G \quad \text{or} \quad K = C_S/C_G \quad (9)$$

The vapor pressure and aqueous solubility data needed for these calculations are reported in our previous publications (for example: references 12-24, 27-34, 36, 38-46 in Supporting Information).

As noted in earlier publications [1,2], three conditions must be met to calculate partition coefficients from solubility data. The conditions are as follows: (1) the same solid phase must be in equilibrium with the saturated solutions in the solvent and in water (in practice this means that there should be no solvate or hydrate formation); (ii) the secondary medium activity coefficient of the solid in the saturated solutions must be unity (or near unity); and (iii) for the solutes that are ionized in aqueous solution, C_w , must refer to the solubility of the neutral form. The second condition would restrict the method to those solutes that are sparingly soluble in water and in the organic solvent. Past applications [2, 5, 31- 34] have show that the Abraham model does accurately describe the solubility of several fairly soluble solutes. For example, Eqns. 2 and 3 described the molar solubility of benzil in 24 organic solvents to within overall standard deviations of 0.124 and 0.109 log units, respectively. [5] Standard deviations for acetylsalicylic acid dissolved in 13 alcohols, 4 ethers and ethyl acetate were 0.123 and 0.138 log units. [31] Flanagan and coworkers [32] further showed that Eqs. 1 and 2 of the Abraham model predicted the experimental solubilities of 1,2,4,5-tetramethylbenzene in 25 different solvents to within an overall standard deviation of 0.15 log units using numerical values of the solute descriptors that had been previously calculated from infinite dilution partition coefficient and chromatographic retention data. Benzil, acetylsalicylic acid and 1,2,4,5-tetramethylbenzene exhibited solubilities exceeding 1 Molar in many of the organic solvents.

Molecular descriptors for all of the compounds considered in the present study are also tabulated in Tables S1 and S2. The tabulated values came from our solute descriptor database,

and were obtained using various types of experimental data, including water-to-solvent partitions, gas-to-solvent partitions, solubility and chromatographic data. [1,18, 19]

3. Results and Discussion

Our search of the published literature yielded 1880 experimental log K values for solutes dissolved in anhydrous (dry) alcohol solvents. The solutes considered cover a reasonably wide range of compound types and descriptor values. The experimental log K data in Table S1 (Supporting Information) were analyzed in accordance with our proposed Abraham model with fragment-specific equation coefficients

$$\log K = \sum_{frag} n_{frag} c_{frag} + \sum_{frag} n_{frag} e_{frag} E + \sum_{frag} n_{frag} s_{frag} S + \sum_{frag} n_{frag} a_{frag} A + \sum_{frag} n_{frag} b_{frag} B + \sum_{frag} n_{frag} l_{frag} L \quad (10)$$

$$(N = 1880, SD = 0.139, R^2 = 1.000 \text{ and } F = 135929)$$

where n_{frag} represents the number of times the given fragment group appears in the alcohol solvent, and the “frag” subscript on each of the six equation coefficients (c, e, s, a, b and l) indicates that the value pertains to a fragment group. As in all group contribution methods, one must decide how to fragment the various molecules into functional groups. Given the molecular structures of the various alcohol solvents (22 monofunctional alcohols and one alkanediol) we opted initially for a very simple fragmentation scheme that involved only five groups. The fragment groups that we have used are: CH₃, CH₂, CH, C and OH. The fragmentation scheme requires the computation of 30 curve-fit constants for both the Abraham model log K and log P equations. More complex fragmentation methods could have been used (such as CH₃, CH₂, CH,

C, OH attached to a primary carbon, OH attached to a secondary carbon, OH attached to tertiary carbon), however, this would introduce additional curve-fit constants. The approach that we have taken is to use only as few curve-fit constants as needed to describe the observed experimental data.

Using our fragmentation scheme the alcohol solvent 2-methyl-1-propanol is composed of 2 CH₃ fragment groups, 1 CH₂ fragment group, 1 CH fragment group and 1 OH fragment group. Numerical values of the fragment-specific equation coefficients are reported in Table 1, along with their respective standard errors (given in parenthesis below each equation coefficient). We do note that the numerical values for the CH₂ in Table 1 are small, and in accord with our earlier observations²⁹ regarding the equation coefficients for the linear primary alcohols (methanol through 1-decanol). Our early study found that the numerical values of the s, a, and b coefficients decreased slightly with increasing alkyl chain length, while the l coefficient increased with alkyl chain length. Here and elsewhere N corresponds to the number of data points, R denotes the correlation coefficient, SD is the standard deviation and F gives the Fisher F statistic. Regression analysis was performed using SPSS statistic software. [34]

Equation 10 is statistically very good and describes an experimental log K database that covers approximately a 36 log unit range to within a standard deviation of SD = 0.139 log units. The number of experimental data points for an individual fragment group ranges from a minimum of 134 log K values for the tertiary C fragment group (found only in 2-methyl-2-propanol and 2-methyl-2-butanol) to 1880 log K values for the OH fragment group, which is found in each alcohol solvent. Figure 1 depicts a plot of experimental log K data versus the calculated values based on Eqn. 10 and the fragment-specific coefficients in Table 1.

As part of our data analyses, we estimated how much descriptive ability was likely to be lost as the result of separating the Abraham model coefficients into fragment-specific values. Abraham model correlations have been reported for 14 of the alcohol solvents considered here. To have a common basis for comparison, the deviations between observed and calculated values were expressed as

$$Dev = \sqrt{\frac{(\log K_{calc} - \log K_{obs})^2}{N - 6}} \quad (11)$$

The results of our computations are summarized in Table 2 for methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-decanol, 2-propanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol and 3-methyl-1-butanol. Examination of the numerical entries reveals that there is a slight loss in descriptive due to the splitting of the equation coefficients into fragment values. For example, our recently updated correlation for gas-to-methanol [29]

$$\begin{aligned} \text{Log K} = & -0.039(0.020) - 0.338(0.044) \mathbf{E} + 1.317(0.059) \mathbf{S} + 3.826(0.057) \mathbf{A} + 1.396(0.062) \mathbf{B} \\ & + 0.773(0.008) \mathbf{L} \end{aligned} \quad (12)$$

based solely on partition coefficients for 146 solutes in only methanol had a deviation of $Dev = 0.142$. The correlation constructed from the fragment-specific equation coefficients in Table 1

$$\begin{aligned} \text{Log K} = & (0.431 - 0.431) + (-0.380 + 0.069) \mathbf{E} + (0.161 + 0.864) \mathbf{S} + (1.609 + 2.289) \mathbf{A} \\ & + (-0.031 + 1.318) \mathbf{B} + (0.558 + 0.264) \mathbf{L} \end{aligned} \quad (13)$$

has a slightly larger deviation of $\text{Dev} = 0.180$ for the same 146 solutes; however, now the equation coefficients are based on partition coefficient data for solutes in the other alcohol solvents as well.

The major advantage of our proposed method is that we can now make predictions for more alcohol solvents. In the past one had to have sufficient experimental data for each alcohol solvent to develop a separate correlation expression. Generally, this required finding or measuring partition coefficients of 40 or 50 solutes in the alcohol under consideration. We have not found sufficient experimental data to develop a log K correlation for 1-nonanol. Now, with the fragment-specific equation coefficients in Table 1 we are able to write a correlation model for 1-nonanol

$$\text{Log K} = -0.088 - 0.183 \mathbf{E} + 0.433 \mathbf{S} + 3.530 \mathbf{A} + 0.543 \mathbf{B} + 0.966 \mathbf{L} \quad (14)$$

that should give reasonably accurate log K predictions. Readers are reminded that the fragment-specific values pertain only to acyclic alcohol solvents, and there are no cyclic alcohols in the database. The tabulated fragment-specific equation coefficients should not be used for other classes of organic compounds, nor should they be used for cyclic alcohols. Our preliminary observations (see Table 3) in applying the tabulated fragment-values to predict the log K values of gases (methane, ethane, ethane, helium, neon, argon, krypton, hydrogen, oxygen, nitrogen carbon dioxide) suggest that one will need to define additional fragment group(s) – either a cyclic ring fragment or perhaps cyclic CH_3 , cyclic CH_2 , etc. fragments. The available log K data for solutes in cyclic alcohols [35-38] is very limited mostly to gases and alkane solutes, and there is not sufficient experimental data at this time to perform a meaningful regression analysis. The database used in the regression analysis did contain only a single alkanediol (ethylene glycol),

and caution needs to be exercised in using the fragment values for alcohols containing more than one OH group.

To further assess the predictive capability of Eqn. 10, we divided the 1880 data points into a training set and test set by selecting every other value. The selection method ensured that every alcohol fragment was evenly distributed between the training and test sets. The selected data points became the training set, and the compounds that were left served as the test set. Analysis of the experimental data in the training set gave the fragment-specific equation coefficients listed in Table S3 (Supporting Information), with $N = 940$, $SD = 0.139$, $R^2 = 1.000$ and $F = 66000$. The training set equation coefficients were then used to predict log K values for the 940 compounds in the test set. For the predicted and experimental values we find $SD = 0.143$, average absolute deviation (AAE) = 0.101 and average error (AE) = -0.004. There is therefore very little bias in the predictions using the Abraham model with the fragment-specific equation coefficients in Table S3 with AE equal to -0.004 log units.

The 1879 experimental water-to-alcohol (dry) partition coefficients were analyzed in similar fashion according to

$$\log P = \sum_{frag} n_{frag} c_{frag} C + \sum_{frag} n_{frag} e_{frag} E + \sum_{frag} n_{frag} s_{frag} S + \sum_{frag} n_{frag} a_{frag} A + \sum_{frag} n_{frag} b_{frag} B + \sum_{frag} n_{frag} v_{frag} V \quad (15)$$

$$(N = 1879, SD = 0.152, R^2 = 0.998 \text{ and } F = 27740)$$

The calculated fragment-specific equation coefficients are given in Table 4, along with their respective standard deviations. Equation 15 is statistically very good with a standard deviation of 0.152 for a log P data base that covers an approximate range of 18 log units. See Figure 2 for

a plot of the calculated values of log P based on Eqn. 15 (equation coefficients in Table 4) against the observed values.

The derived water-to-alcohol correlations were validated by dividing the 1879 experimental data points into a training set and a test set as before. Analysis of the experimental data set gave the fragment-specific equation coefficients that were tabulated in Table S4 (Supporting Information), with $N = 940$, $SD = 0.152$, $R^2 = 0.998$ and $F = 13666$. The training set equation was then used to predict log P values for the 939 compounds in the test set. For the predicted versus experimental values, we find that $SD = 0.155$, $AAE = 0.113$ and $AE = -0.003$. There is therefore very little bias in the predictions using the Abraham model with the fragment-specific equation coefficients from Table S4 with AE equal to -0.003 log units.

Finally, water-to-alcohol (dry) correlations have been reported in the literature for 13 of the alcohols considered here. The published alcohol-specific correlations provide a benchmark for us to use in assessing how much descriptive ability might be lost as the result of splitting the equation coefficients into fragment values. In Table 5 we have assembled the deviations between the observed and calculated values based on Eqn. 15, and the deviations that were reported at the time each benchmark alcohol-specific correlation was published. Examination of the tabulated values indicates that there is a small loss in descriptive ability due to splitting of the solvent coefficient into fragment values, an average standard deviation of $SD = 0.141$ for the alcohol-specific correlations versus $SD = 0.154$ for the correlations employing fragment-specific values. Based on the comparisons presented above, the simple fragmentation scheme (CH_3 , CH_2 , CH , C and OH groups) does adequately describe the observed experimental data. There is no reason at the present time to introduce more fragment-groups and curve-fit parameters into the model.

5. Conclusion

Our methodology of splitting the Abraham model equation coefficients into fragment-specific values, which was first illustrated with room temperature ionic liquids using cation-specific and anion-specific coefficients [20-23], has been successfully extended to alcohol solvents. Fragment-specific equation coefficients have been calculated for the CH₃, CH₂, CH, C and OH functional groups. The fragment-specific equation coefficients can be summed to yield Abraham model correlations for predicting partition coefficients describing solute transfer from the gas phase to an anhydrous alcohol solvent, and for predicting partition coefficients that describe solute transfer from water to an anhydrous alcohol solvent. The derived correlation equations were found to describe the log K and log P values of more than 1850 solute-alcohol solvent combinations to within standard deviations of SD = 0.14 and SD = 0.15 log units, respectively.

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Table 1. Fragment-Specific Equation Coefficients for the Abraham Model for Describing the Gas-to-Alcohol (Dry) Partition Coefficients of Solutes at 298 K

Fragment Group	c	e	s	a	b	l
CH ₃	0.431	-0.380	0.161	1.609	-0.031	0.558
	(0.018)	(0.040)	(0.053)	(0.054)	(0.076)	(0.007)
CH ₂	-0.011	0.016	-0.074	-0.046	-0.093	0.018
	(0.003)	(0.005)	(0.006)	(0.007)	(0.008)	(0.001)
CH	-0.448	0.330	-0.440	-1.649	-0.114	-0.500
	(0.026)	(0.056)	(0.076)	(0.074)	(0.097)	(0.010)
C	-0.800	0.642	-0.644	-3.096	-0.366	-1.033
	(0.047)	(0.104)	(0.140)	(0.141)	(0.187)	(0.017)
OH	-0.431	0.069	0.864	2.289	1.318	0.264
	(0.015)	(0.036)	(0.046)	(0.049)	(0.071)	(0.006)

Table 2. Comparison of the Predictive Ability of the log K Alcohol-Specific Abraham Model Correlations Versus Abraham Model Correlations Using Fragment-Specific Equation Coefficients

Alcohol Solvent	Deviation ^a	
	Alcohol-Specific Eqn.	Fragment-Specific Eqn.
Methanol	0.142	0.180
Ethanol	0.149	0.159
1-Propanol	0.137	0.145
1-Butanol	0.151	0.165
1-Pentanol	0.108	0.119
1-Hexanol	0.119	0.124
1-Heptanol	0.086	0.088
1-Octanol	0.128	0.139
1-Decanol	0.100	0.126
2-Propanol	0.122	0.131
2-Butanol	0.138	0.139
2-Methyl-1-propanol	0.144	0.155
2-Methyl-2-propanol	0.135	0.136
3-Methyl-1-butanol	<u>0.124</u>	<u>0.127</u>
Average	0.127	0.138

$$^a Dev = \sqrt{\frac{(\log K_{calc} - \log K_{obs})^2}{N - 6}}$$

Table 3. Comparison of the Experimental Log K Data for Alkane Solutes and Gases in Cyclohexanol Versus Calculated Values Based on the Abraham Model and Fragment-Specific Equation Coefficients Given in Table 1

Solute	Log K _{calc}	Log K _{obs}	[Ref]
Helium	-0.677	-1.951	SDS ^a
Neon	-0.701	-1.770	SDS ^a
Argon	-0.831	-0.902	SDS ^a
Krypton	-0.901	-0.401	SDS ^a
Hydrogen	-0.756	-1.409	SDS ^a
Oxygen	-0.694	-0.826	37
Nitrogen	-0.789	-1.202	36
Carbon dioxide	-0.831	0.020	36
Methane	-0.885	-0.528	36

^a IUPAC Solubility Data Series

Table 4. Fragment-Specific Equation Coefficients for the Abraham Model for Describing the Hypothetical Water-to-Alcohol (Dry) Partition Coefficients of Solutes at 298 K

Fragment Group	c	e	s	a	b	v
CH ₃	0.342	0.096	-0.687	-0.109	-2.273	2.478
	(0.027)	(0.042)	(0.063)	(0.058)	(0.094)	(0.033)
CH ₂	-0.030	0.023	-0.043	-0.044	-0.110	0.070
	(0.003)	(0.005)	(0.007)	(0.007)	(0.009)	(0.004)
CH	-0.421	-0.104	0.489	0.089	2.049	-2.237
	(0.038)	(0.056)	(0.084)	(0.078)	(0.115)	(0.046)
C	-0.720	-0.261	1.193	0.273	4.021	-4.618
	(0.067)	(0.108)	(0.159)	(0.150)	(0.222)	(0.076)
OH	-0.099	0.266	-0.214	0.404	-1.204	1.292
	(0.024)	(0.038)	(0.058)	(0.054)	(0.089)	(0.030)

Table 5. Comparison of the Predictive Ability of the log K Alcohol-Specific Abraham Model Correlations Versus Abraham Model Correlations Using Fragment-Specific Equation Coefficients

Alcohol Solvent	Percent Deviation ^a	
	Alcohol-Specific Eqn.	Fragment-Specific Eqn.
Methanol	0.162	0.201
Ethanol	0.161	0.170
1-Propanol	0.151	0.162
1-Butanol	0.162	0.180
1-Pentanol	0.124	0.133
1-Hexanol	0.140	0.142
1-Heptanol	0.113	0.120
1-Decanol	0.126	0.162
2-Propanol	0.162	0.170
2-Butanol	0.128	0.135
2-Methyl-1-propanol	0.144	0.157
2-Methyl-2-propanol	0.162	0.163
3-Methyl-1-butanol	<u>0.103</u>	<u>0.111</u>
Average	0.141	0.154

$$^a Dev = \sqrt{\frac{(\log K_{calc} - \log K_{obs})^2}{N - 6}}$$

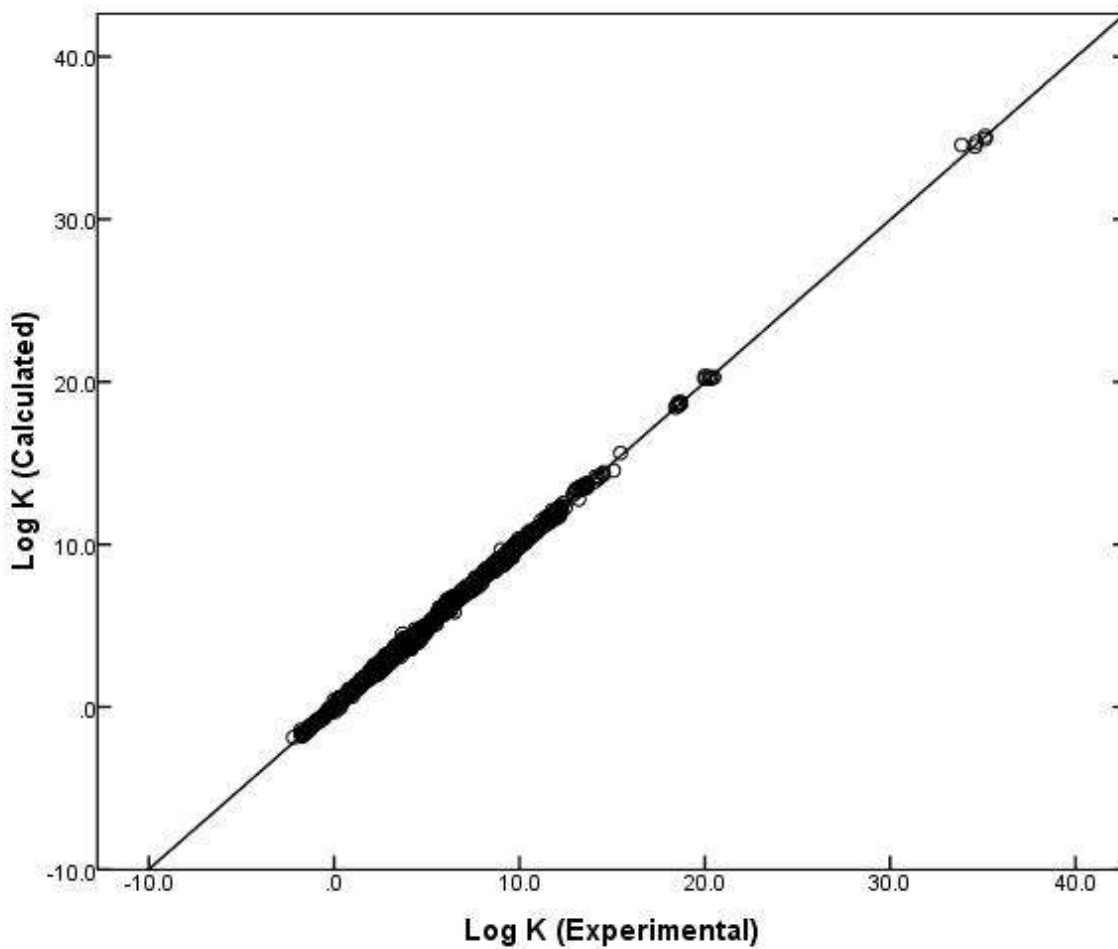


Figure 1. Comparison of experimental log K data and calculated values based on Eqn. 10 and the fragment-specific equation coefficients given in Table 1.

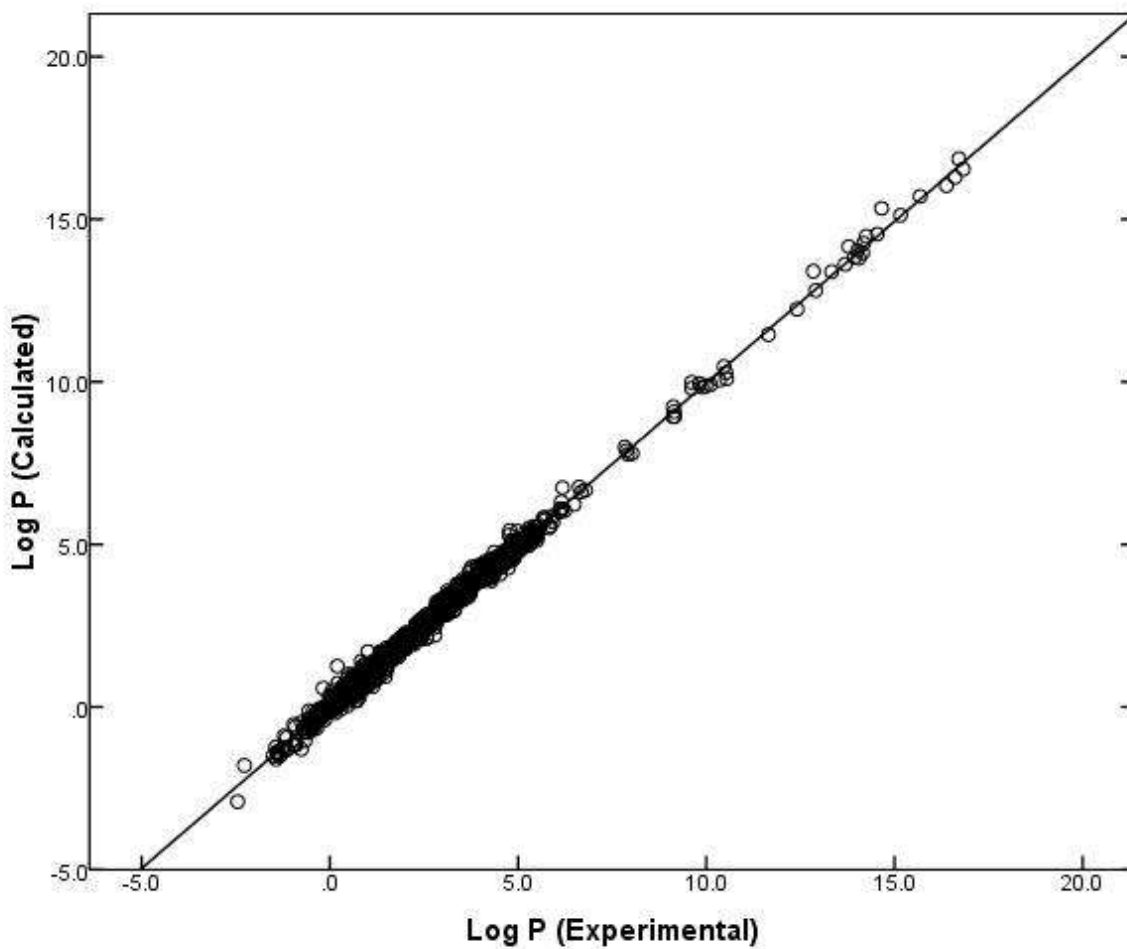


Figure 2. Comparison of experimental log K data and calculated values based on Eqn. 15 and the fragment-specific equation coefficients given in Table 4.