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Evaluation of Three Prediction Methods for Partitioning Coefficients of Organic Solutes between a Long-Chain Aliphatic Alcohol and the Gas Phase as a Function of Temperature

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Temperature-dependent experimental hexadecan-1-ol/air partition coefficients of numerous organic solutes are regressed against molecular interaction parameters to derive a linear solvation energy relationship (LSER) for each experimental temperature. The system constants derived by these regressions are linearly related to reciprocal absolute temperature, allowing their extrapolation to 298.15 K and the establishment of a LSER equation for the hexadecan-1-ol/air partition coefficients at 298.15 K. This equation yields predictions comparable to those of another LSER equation for that parameter that is independently derived by extrapolating the system constants of smaller aliphatic alcohols to the chain length of hexadecan-1-ol. This confirms that the solvation properties of the long-chain alkanols can be extrapolated from those of smaller normal alcohols. Hexadecan-1-ol/air partition coefficients for the same solutes are also predicted using SPARC and calculated from vapor pressure data from the literature and activity coefficients in hexadecan-1-ol predicted by UNIFAC. The SPARC- and UNIFAC-predicted partition coefficients agree well with each other, and also the agreements between predictions and measurements are acceptable considering experimental uncertainty. A comparison of measured and predicted activity coefficients in hexadecan-1-ol reveals that they are not correlated, although they are in the same range and have a similar average. The predictions of the partition coefficients simply succeed because their variability is determined by vapor pressure rather than the activity coefficient, which only varies within an order of magnitude.

Introduction

Accurate data of the partitioning characteristics of organic solutes between organic solvents and the gas phase at different temperatures are required for many applications, but experimental measurements are always time-consuming and expensive. Considering the large number of potential solvents and solutes, it is unrealistic that experimental data for all systems of interest could be established experimentally. Therefore, there is a need for reliable methods estimating such phase partitioning equilibria as a function of temperature. Among the methods commonly used to estimate the solvation properties of organic chemicals are the UNIFAC (UNIQUAC Functional Group Activity Coefficients) group-contribution method by Fredenslund et al.,[1] the SPARC system by Hilal et al.,[2] and the Linear Solvation Energy Relationship (LSER) approach by Kamlet, Abraham, and coworkers.[3,4] To our knowledge, no comparative evaluation of these prediction methods has ever been conducted.

LSERs are among the most commonly used poly-parametric linear free energy relationship (PP-LFER) approaches for the analysis and prediction of solute partitioning in chemical and biochemical systems. This approach has been used to correlate and predict solute properties in numerous systems, including many of environmental interest.[5,6] For processes involving gas to condensed phase transfer, the LSER equation takes the form:

$$\log \mathrm{SP} = c + rR + sS + aA + bB + l \log L_{16} \qquad (1)$$

The dependent variable, log SP, is the solvation property of interest, and R, S, A, B, and $\log L_{16}$ are solute descriptors representing the excess molar refraction, dipolarity/polarizability, hydrogen bond acidity, hydrogen bond basicity, and the logarithm of 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, give information on the polarizability, dipolarity/polarizability, hydrogen bond basicity, and hydrogen bond acidity of the solvent phase, respectively. The l coefficient describes the phase lipophilicity and is the result of cavity and general dispersion interaction effects.

SP in eq 1 refers to the solvation property at one particular temperature. Fairly limited information on the temperature dependence of system constants is available, because not for many solvent systems is there a sufficient number of measured partitioning coefficients to allow for the calculation of system constants at different temperatures. Because of the ease of measuring gas chromatographic (GC) capacity factors at different temperatures, the temperature dependence of the system constants for various stationary phases used in GC columns is better established. Li and Carr[7] indicated that such system constants show a linear relationship against reciprocal absolute temperature:

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

where X stands for a system constant, and X_A and X_B are the

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intercept and slope of the regression, respectively. Based on such equations, it should be possible to derive LSER equations outside the measured temperature range.

In a companion paper, we report on the measurement of the hexadecan-1-ol/air partitioning coefficients $K_{16OH/A}$ for a diverse set of organic compounds at a number of temperatures.[8] The current study has two main objectives. We first used the LSER approach to explain the variability between the hexadecan-1-ol/air partition coefficients measured for different organic solutes. Specifically, we used multi-variate linear regression analysis to fit the measured log $K_{16OH/A}$ data to the solute descriptors using eq 1. By having determined experimental $K_{16OH/A}$ data at different temperatures,[8] we also had the opportunity to explore the temperature dependence of the system constants for the hexadecan-1-ol/air system.

We further used three different methods to predict $K_{16OH/A}$ for the solutes and evaluated the performance of these prediction methods by comparing the predictions with the experimental values. The three methods are as follows:

(1) LSER Method. No LSER for the prediction of $K_{16OH/A}$ existed prior to this work. However, Abraham et al.[9] had previously presented LSER equations to describe the solvation properties of the normal alcohols up to a length of 10 carbon atoms. By extrapolating the relationship between the system constants and the carbon chain length N_C for short-chain normal alcohols to $N_C = 16$, we derived an LSER for $K_{16OH/A}$ that is entirely independent from the experimental data we have determined and that can be used to predict $K_{16OH/A}$. In addition to directly comparing measured and predicted $K_{16OH/A}$ values for numerous organic solutes, we can also compare the system constants for the hexadecan-1-ol/air system derived by extrapolation with the ones we derived from the experimental data.

(2) UNIFAC Method. The UNIFAC method, originally developed by Fredenslund et al.[1] and later revised and extended in a series of papers,[10−14] predicts liquid-phase activity coefficients, γ_S. UNIFAC divides the activity coefficients into a combinatorial term that depends on the volume and surface area of each molecule and a residual term that is a result of the energies of interaction between the molecules. Both the combinatorial and residual terms are derived from group-contribution methods.[15] If the liquid-state vapor pressure P_L of a compound is known, the solvent/air partition coefficient, here $K_{16OH/A}$, can be calculated from the UNIFAC-predicted activity coefficient γ_{16OH} using:

$$K_{16OH/A} = RT/(V_{16OH}\gamma_{16OH}P_L) \tag{3}$$

where V_{16OH} is the molar volume of hexadecan-1-ol at infinite dilution at a certain temperature T. At 298.15 K, V_{16OH} is 0.296 L/mol.

(3) SPARC Method. The SPARC model is another method often used to predict physical−chemical properties for chemicals. It links the molecular descriptors predicted by Perturbed Molecular Orbital theory, such as charge distribution and molecular polarizability, with linear free energy relationships to calculate thermodynamic and thermal properties.[16] It considers the four categories of solute−solvent interactions: dispersion, induction, dipole−dipole, and H-bonding. For vapor−liquid equilibrium, SPARC predicts the vapor pressure and activity coefficient of the solute in the solvent phase at infinite solution to calculate the partition coefficient (i.e., Henry's law constant) using an approach similar to eq 3. Details are given by Hilal et al.[16,17]

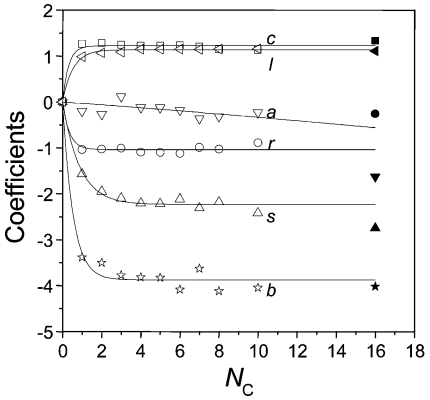

Figure 1. Comparison of the LSER system constants for hexadecan-1-ol/air from eq 11 (filled markers) with those of other normal alkanols[9] (open markers) based on the difference to the system constants for the gas−water partition coefficient. N_C represents the carbon number, for water, $N_C = 0$.

Materials and Methods

The measurement of the hexadecan-1-ol/air partition coefficients ($K_{16OH/A}$), which form the basis of the data analysis presented here, is described in a companion paper.[8] Although the $K_{16OH/A}$ values at 298.15 K reported in that paper were derived by extrapolation from data measured at higher temperatures, they are referred to as measured data when being compared with data predicted theoretically.

LSER Analysis of Hexadecan-1-ol/Air Partitioning Data. LSER solute descriptors for the investigated solutes were taken from the literature[18−22] and are listed in Table SP-1 in the Supporting Information. B and log L_{16} showed the largest intercorrelation between the descriptors, with an R^2 of 0.43. The next largest intercorrelation (R^2 is 0.37) is that between R and log L_{16}. Although those intercorrelations are not very strong, they may still affect the regression results. The measured partitioning data at five experimental temperatures (343.15 K, 353.15 K, 363.15 K, 373.15 K, and 383.15 K) from Xiao et al.[8] were regressed against these descriptors using SPSS 12.0 for Windows (SPSS Inc.). A stepwise regression method was used to test the significance of all parameters. Only the correlation between the S parameter and the partition coefficients of the compounds of interest was insignificant at all temperatures. For consistency and comparison, the S parameter was excluded from the regressions, whereas all the other solute descriptors were included. Resistant regression (least median square method) used in the temperature dependence analysis was conducted using R 2.1.1 (The R development core team).

Derivation of an LSER to Predict Hexadecan-1-ol/Air Partition Coefficients at 298.15 K. Figure 1, adapted from Abraham et al.,[9] compares the LSER system constants for a number of normal alkanes. Rather than directly displaying the system constants, Figure 1 plots the difference between the system constants for the different alcohols and water as a function of carbon number. This figure clearly shows the changing trend of the solvation properties of aliphatic alcohols compared with water, as the carbon number increases. 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 electron pairs effect, dipolarity/polarizability interaction, and hydrogen bond interaction between solute and alcohols are much weaker than that between solute and water, whereas the cavity effect and the solute/alcohol dispersion interaction are much stronger. The figure also shows that the differences between the solvation characteristic of the normal alcohols become smaller with increasing length of the aliphatic chain. LSER-based predictions for log $K_{16OH/A}$, which are completely independent from the measurements presented in Xiao et al.,[8] were derived by fitting nonlinear exponential growth curves to the relationships between the system constant differences for the short alcohols ($N_C < 10$) and carbon chain length displayed in Figure 1:

$$y = y_0 - y_0 \exp(\mathrm{NC}/t) \tag{4}$$

The resulting fitting curves are included in Figure 1. System constants for hexadecan-1-ol/air were then derived by extrapolating these relationships to $N_C = 16$. The resulting LSER regression is

$$\log K_{16OH/A} \text{ at } 298.15\text{K} = -0.03482 - 0.1548R + 0.4246S + 3.4932A + 0.9396B + 0.8976 \log L_{16} \tag{5}$$

This equation was used to predict log $K_{16OH/A}$ for the organic solutes that had been studied by Xiao et al.[8]

Prediction of Hexadecan-1-ol/Air Partition Coefficients Using UNIFAC and SPARC. SPARC only requires the user to supply the molecular structure of the solute in the form of CAS Registry Number or SMILES notation. These were entered into the SPARC on-line calculator (http://ibmlc2.chem.uga.edu/sparc/) to predict the Henry's law constant for hexadecan-1-ol. The results given by the calculator were converted to SI units (Pa/(mol·m^3)) for further analysis.

UNIFAC calculates the activity coefficient based on mole fraction of chemicals and the interaction between different functional groups. All the chemicals are considered a collection of functional groups, and the volume and surface area of the molecule can be calculated from the sum of all groups occurring in a molecule. Structure information was input into public domain computer software, UNIFACAL (Version 3.0; Bruce Choy and Danny Reible). The calculations were based on Hansen et al.'s group interaction parameter table. Experimentally, very low concentrations were used to measure the partition coefficient,[8] thus, a mole fraction of 0.0001 was assumed for all chemicals of interest.

Results and Discussions

Description of the Hexadecan-1-ol/Air Partitioning Data with Linear Solvation Energy Relationships. The system constants of the LSERs for log $K_{16OH/A}$ at different temperature are listed in Table 1. Partitioning coefficients calculated from these fitted regressions are plotted against the measured values in Figure 2, showing that the LSER regressions describe the partitioning coefficients at 343.15 K to 383.15 K well. All data points are close to the diagonal 1:1 lines, and most are well within the 95 % confidence limit. The system constants in Table 1 reveal that the partition coefficients are strongly correlated to a solute's log L_{16} (i.e., hexadecane/air partition coefficient), which means that the hexadecan-1-ol/air partitioning equilibrium of a solute is strongly affected by the cavity effect and dispersive solute/phase interactions. The solute hydrogen acidity and basicity, A and B, also show a significant correlation with the partition coefficient. This confirms that hexadecan-1-ol serves as both hydrogen donor and acceptor. The relative size of the standardized system constants (β), which are the regression coefficients derived from standardized dependent and variables, relays information on the relative importance of different types of solute/solvent interactions: $\beta(l) > \beta(a) > \beta(b) \approx \beta(r) > \beta(s)$ (not significant), suggesting that the strength of the interaction decreases from dispersive interactions, hydrogen bonding, solute/solvent σ/π electron pair interaction to solute/solvent dipolarity/polarizability interaction.

Table 1. Regression and Statistical Parameters of the LSERs Analysis of Hexadecan-1-ol/Air Partition Coefficients at Several Temperatures

		unstandardized coefficients		standardized coefficients		
		B	SE	β	*t*	sig.
343.15 K	*c*	0.2290	0.1076		2.1285	0.041
	l	0.6628	0.0264	1.0912	25.0668	0.000
	a	1.7441	0.1448	0.4470	12.0455	0.000
	b	0.5428	0.1183	0.1850	4.5883	0.000
	r	0.3695	0.0646	0.2039	5.7238	0.000
353.15 K	*c*	0.2766	0.1072		2.5806	0.014
	l	0.6155	0.0258	1.0909	23.8814	0.000
	a	1.5985	0.1453	0.4258	10.9983	0.000
	b	0.4771	0.1196	0.1721	3.9876	0.000
	r	0.3411	0.0634	0.1980	5.3777	0.000
363.15 K	*c*	0.1939	0.1065		1.8214	0.0771
	l	0.6020	0.0252	1.0811	23.8630	0.0000
	a	1.2603	0.1658	0.2920	7.5999	0.0000
	b	0.5831	0.1246	0.2164	4.6815	0.0000
	r	0.2770	0.0618	0.1634	4.4825	0.0001
373.15 K	*c*	0.3216	0.1049		3.0668	0.004
	l	0.5396	0.0256	1.0866	21.0880	0.000
	a	1.4494	0.1439	0.4396	10.0686	0.000
	b	0.4057	0.1171	0.1632	3.4639	0.001
	r	0.2693	0.0639	0.1780	4.2177	0.000
383.15 K	*c*	0.2071	0.1178		1.7582	0.0896
	l	0.5398	0.0284	1.1091	18.9777	0.0000
	a	1.4798	0.1709	0.4621	8.6597	0.0000
	b	0.4314	0.1477	0.1637	2.9210	0.0068
	r	0.2247	0.0789	0.1395	2.8462	0.0082

Temperature Dependence of the LSER System Constants. Figure 3 plots the system constants against reciprocal absolute temperature. In agreement with eq 2 advocated by Li and Carr,[7] most of the relationships are linear, although some points significantly depart from the linear trends. To overcome this outlier problem, a least median square technique was used to linearly fit the data. The fitting results are

$$c = -395.393/(T/\text{K}) + 1.389 \tag{6}$$

$$l = 525.867/(T/\text{K}) - 0.872 \tag{7}$$

$$a = 1258.192/(T/\text{K}) - 1.943 \tag{8}$$

$$b = 585.026/(T/\text{K}) - 1.171 \tag{9}$$

$$r = 427.660/(T/\text{K}) - 0.873 \tag{10}$$

By extrapolating each of these regressions to lower temperature, system constant at 298.15 K can be estimated, and a LSER equation for hexadecan-1-ol/air partition coefficient at 298.15 K can be assembled:

$$\log K_{16OH/A} \text{ at } 298.15\text{K} = 0.06285 + 0.5611R + 2.2770A + 0.7912B + 0.8921 \log L_{16} \tag{11}$$

We now have two LSER equations for the calculation of log $K_{16OH/A}$ at 298.15 K: eq 5 derived by extrapolation of the system constants for shorter alcohols reported by Abraham et al.,[9] and eq 11 derived from the data measured at higher temperatures.[8] The differences between the estimated system constants for hexadecan-1-ol at 298.15 K in eq 11 (while let $s = 0$) and those for water[5] are included on the right side of Figure 1. It can be seen that most of the system constants are close to the exponential curves, with only the a and r coefficients showing larger differences. Considering the uncertainty in these system constants introduced by the extrapolation over fairly large ranges

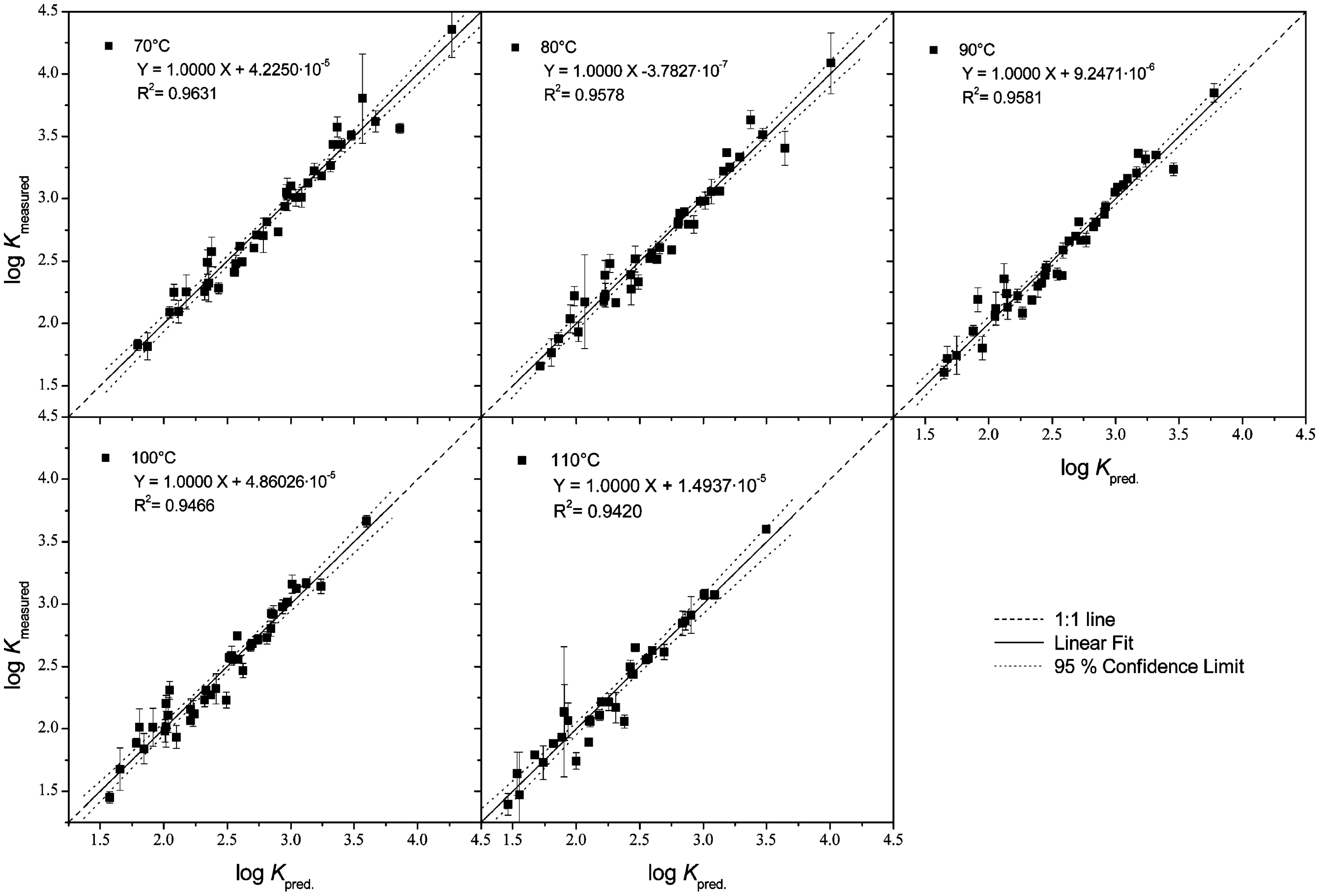

Figure 2. Comparison of measured log $K_{16OH/A}$ values at different temperatures[8] with the results of the LSER regressions listed in Table 1.

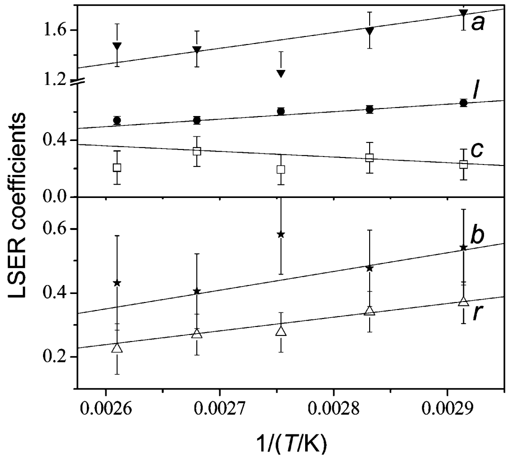

Figure 3. Temperature dependence of the LSER system constants for hexadecan-1-ol/air partitioning.

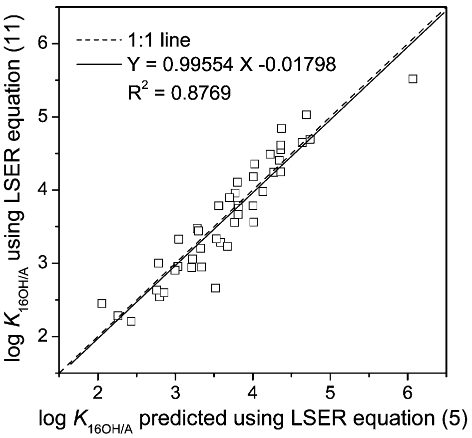

Figure 4. Comparison of hexadecan-1-ol/air partition coefficients predicted by LSER (eqs 5 and 11).

of temperature or N_C, results from this study are consistent with the results of previous research on the solvation properties of normal alcohols.

In addition to directly comparing the system constants in eqs 5 and 11, we can compare log $K_{16OH/A}$ values calculated with either equation for the organic solutes studied by Xiao et al.[8] This is done in Figure 4, which shows that these two equations give comparable results. A paired two sample *t*-test confirmed that there is no significant difference between these two sets of data ($t = 0.816$, $p = 0.419$, Table 3).

Comparative Evaluation of the Predictions of log $K_{16OH/A}$ at 298.15 K. Table 2 lists the log $K_{16OH/A}$ values predicted by LSER (eq 5), by SPARC, and by UNIFAC. The latter are calculated from the activity coefficients predicted by UNIFAC using eq 3 and P_L values from the literature.[8] Figure 5 compares the experimental log $K_{16OH/A}$ at 298.15 K with those calculated from the three different prediction methods. All three prediction methods show reasonable agreement with the measured data with a slope close to 1 and R^2 values of approximately 0.80 or above. Most of the data points are located close to the 1:1 line. Table 3 gives the results of paired two sample *t*-test comparing predicted and experimental values at 298.15 K. Interestingly, although the SPARC predictions and measurements show the highest correlation with each other, only the difference between these two sets is significant at the $\alpha = 0.05$ level.

Figure 6 compares the three log $K_{16OH/A}$ predictions with each other, indicating good agreement between the values calculated

Table 2. Hexadecan-1-ol/Air Partition Coefficients $K_{16OH/A}$ and Activity Coefficients in Hexadecan-1-ol, γ_{16OH}, Calculated by LSER (eqs 5 and 11) and Predicted by SPARC and UNIFAC

	log $K_{16OH/A}$				γ_{16OH}		
chemicals	eq 5	eq 11	UNIFAC (eq 3)	SPARC	measured[8]	UNIFAC	SPARC (eq 3)
nonane	3.809	3.793	4.008	3.870	3.048	1.438	1.756
decane	4.274	4.243	4.491	4.362	2.122	1.580	1.862
undecane	4.740	4.694	4.966	4.856	2.167	1.721	1.971
cyclooctane	4.131	3.982	3.964	3.950	1.242	1.208	1.343
1-nonene	3.814	3.752	3.936	3.852	1.339	1.360	1.764
1-heptyne	3.328	3.204	2.813	2.952	0.833	1.716	1.415
1-octyne	3.810	3.666	3.413	3.409	0.883	1.887	1.484
propan-1-ol	3.672	3.229	3.391	3.228	2.326	1.214	1.148
propan-2-ol	3.342	2.950	3.077	3.008	3.121	1.213	1.322
butan-1-ol	4.001	3.786	3.910	3.729	1.550	1.153	1.062
2-methyl-1-propanol	4.013	3.559	3.685	3.513	1.078	1.152	1.293
octan-1-ol	6.068	5.517	5.858	5.781	3.084	1.042	0.929
propyl ether	3.223	3.059	3.057	3.081	0.884	0.880	0.910
isopropyl ether	2.759	2.633	2.667	2.379	1.242	0.906	1.978
tetrahydrofuran	3.034	2.956	2.734	2.595	0.389	0.713	0.866
1,4-dioxane	3.528	3.334	3.245	3.290		0.967	0.854
acetone	2.051	2.451	2.297	2.245	0.387	1.369	1.538
2-butanone	2.858	2.600	2.689	2.691	1.310	1.347	1.270
3-methyl butan-2-one	3.213	2.943		2.969		1.345	1.301
cyclopentanone	3.765	3.557	3.710	3.353	2.217	1.049	1.664
methyl acetate	2.429	2.203	2.388	2.127	1.073	1.186	2.589
ethyl acetate	2.799	2.543	2.753	2.537	1.926	1.173	1.999
isobutyl acetate	3.586	3.284	3.419	3.231	0.638	1.216	2.110
1,2-dichloroethane	2.995	2.906	2.819	2.682	1.402	1.213	1.379
1,1,2,2-tetrachloroethane	4.362	4.248	3.898	3.889	0.558	1.333	1.755
1-iodopropane	3.044	3.329	3.081	3.134	1.179	1.208	1.056
1,1,2-trichlorotrifluorethane	2.258	2.284		1.861	1.472		1.853
2,2,2-trifluoroethanol	3.519	2.659	2.815	3.500	1.428	1.349	0.233
benzene	2.783	3.001	2.873	2.681	0.419	0.884	1.270
toluene	3.282	3.477	3.332	3.237	0.845	1.028	1.158
p-xylene	3.773	3.958	3.839	3.818	0.725	1.115	1.111
1,2,4-trimethylbenzene	4.363	4.555	4.411	4.424	0.585	1.160	1.046
ethylbenzene	3.702	3.896	3.751	3.679	1.086	1.160	1.101
styrene	3.803	4.106	4.215	3.827	0.676	0.579	1.381
chlorobenzene	3.563	3.783	3.707	3.528	1.211	1.039	1.280
1,2-dichlorobenzene	4.362	4.614	4.475	4.467	0.260	1.390	1.264
1,3-dichlorobenzene	4.224	4.488	4.292	4.281	0.865	1.390	1.067
bromobenzene	4.027	4.354	3.845	4.009	0.139	2.141	1.552
iodobenzene	4.374	4.841	4.302	4.592		3.103	2.068
4-fluorotoluene	3.298	3.444	3.366	3.493	1.295	1.271	0.889
anisole	4.008	4.183	4.027	3.760	1.670	1.708	2.009
benzaldehyde	4.343	4.407	4.557	4.180	2.047	1.374	2.648
indan	4.640	4.651	4.491	4.578	0.405	1.370	1.811
indene	4.693	5.029		4.423		1.431	2.045

Table 3. Results of Paired Two Sample *t*-Tests Comparing Various Sets of Predicted and Measured Hexadecan-1-ol/Air Partition Coefficients[a]

	paired differences							
				95 % confidence interval of the difference				
	mean	SD	SE mean	lower	upper	*t*	df	sig. (2-tailed)
	Compared at 298.15 K							
ref 8, eq 5	−0.016	0.378	0.058	−0.133	0.102	−0.271	41	0.788
ref 8, eq 11	0.027	0.245	0.038	−0.050	0.103	0.707	41	0.484
ref 8, UNIFAC	0.073	0.322	0.051	−0.031	0.178	1.424	38	0.163
ref 8, SPARC	*0.141*	*0.304*	*0.047*	*0.046*	*0.236*	*3.005*	*41*	*0.005*
eq 5, eq 11	0.034	0.280	0.042	−0.051	0.119	0.816	43	0.419
eq 5, UNIFAC	0.071	0.230	0.036	−0.001	0.144	1.988	40	0.054
eq 5, SPARC	*0.150*	*0.208*	*0.031*	*0.087*	*0.213*	*4.801*	*43*	*0.000*
eq 11, UNIFAC	0.032	0.212	0.033	−0.035	0.099	0.974	40	0.336
eq 11, SPARC	*0.116*	*0.232*	*0.035*	*0.045*	*0.186*	*3.311*	*43*	*0.002*
UNIFAC−SPARC	*0.068*	*0.190*	*0.030*	*0.008*	*0.128*	*2.275*	*40*	*0.028*
	Compared at Real Experimental Temperature Range							
ref 8, UNIFAC	*0.214*	*0.151*	*0.014*	*0.187*	*0.242*	*15.269*	*115*	*0.000*
ref 8, SPARC	*0.193*	*0.176*	*0.012*	*0.168*	*0.217*	*15.602*	*202*	*0.000*
UNIFAC−SPARC	*−0.044*	*0.143*	*0.012*	*−0.068*	*−0.020*	*−3.616*	*138*	*0.000*

[a] The numbers in italic indicate that there are significant differences between the two sets of samples.

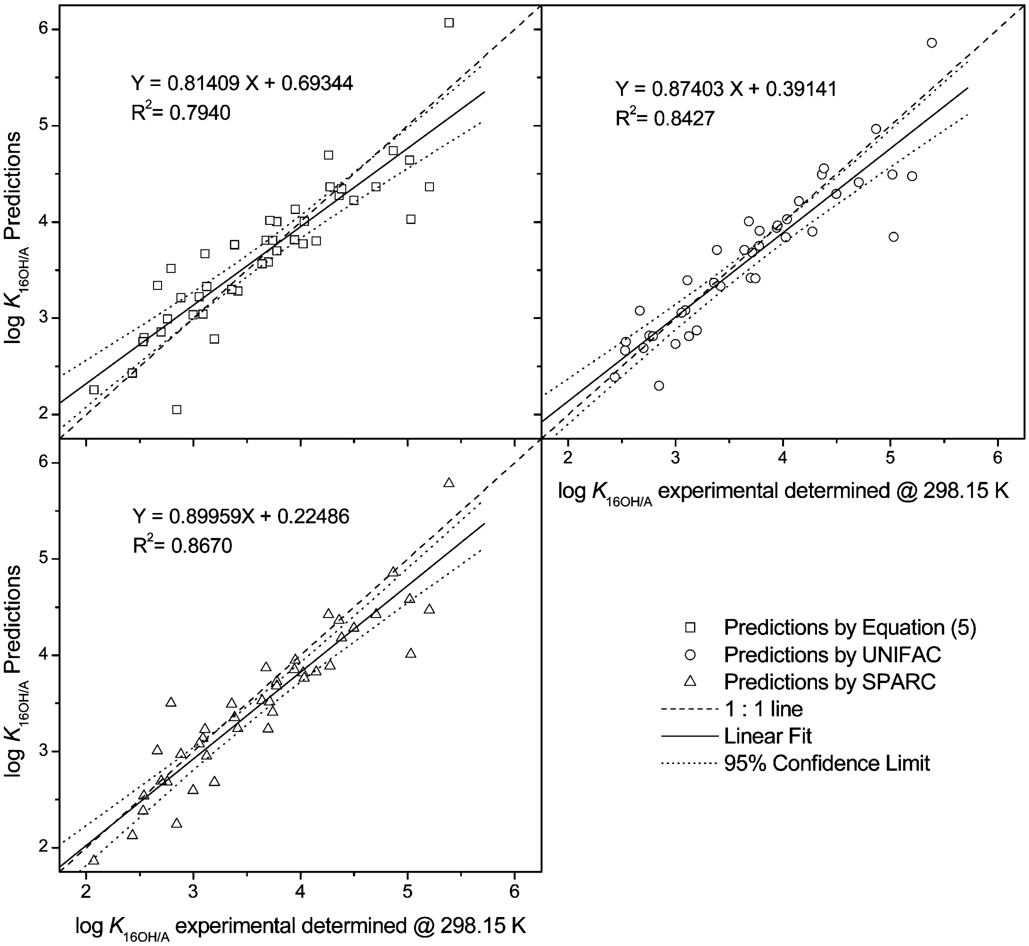

Figure 5. Comparison of the experimentally determined hexadecan-1-ol/air partition coefficients at 298.15 K[8] with the predictions from LSER (eq 5), UNIFAC, and SPARC.

by LSER (eq 11), UNIFAC, and SPARC. Table 3 gives again the results of paired two sample *t*-test comparing the values obtained by the three prediction methods at 298.15 K. At the $\alpha = 0.05$ level only the difference between SPARC and the other methods is significant. Interestingly, the prediction methods agree better with each other than with the measured data. The correlation coefficients between the different predictions are usually higher than those involving measured data. Furthermore, the standard deviations and standard mean error within predictions is also smaller.

Considering that the measured $K_{16OH/A}$ values had shown a strong correlation with vapor pressure,[8] it is conceivable that the apparent success of the prediction methods may be more based on a correct prediction of the volatility of the solutes, than on a correct prediction of the solvation in hexadecan-1-ol. In the case of UNIFAC, which does not predict P_L, this can be checked by directly comparing the activity coefficient predicted by UNIFAC with those derived from the measured data.[8] Activity coefficients were further calculated from P_L and $K_{16OH/A}$, both predicted by SPARC, based on eq 3 (see Table 2). Even though the predicted and the measured activity coefficient cover a similar overall range (0.6 to 3.1 for UNIFAC vs 0.2 to 2.6 for SPARC vs 0.1 to 3.1 from measurements) and have a similar average (1.3 ± 0.4 for UNIFAC, 1.5± 0.5 for SPARC, and 1.3 ± 0.8 for measurements), they are not correlated with each other (Figure 7). Even the two sets of predicted values show little relationship with each other ($R^2 = 0.12$). The agreement between the UNIFAC-derived $K_{16OH/A}$ and the measured values noted earlier (Figure 5, Table 3) is therefore largely due to the high degree of correlation between the measured $K_{16OH/A}$ and P_L data compiled from the literature and has very little to do with the UNIFAC predictions. In fact, a prediction of $K_{16OH/A}$ based on P_L and a constant γ_{16OH} of 1 would have yielded comparably good results. Similarly, we may conclude that the reasonably good agreement between the SPARC-predicted $K_{16OH/A}$ and the measured values is due to the successful prediction of the vapor pressure of the solutes.

Comparative Evaluation of the Predictions of Log $K_{16OH/A}$ at the Temperatures of the Experiments. The experimental values of $K_{16OH/A}$ at 298.15 K used in the above evaluation of the predictions is a value obtained by extrapolation of data measured at much higher temperatures and therefore has relatively poor precision. Because of the high uncertainty of the $K_{16OH/A}$ values at 298.15 K, we should be cautious to derive firm conclusions from the lack of a relationship between the γ_{16OH} derived from these values and those predicted by UNIFAC and SPARC. It is preferable to evaluate predictions of $K_{16OH/A}$ at the actual temperature of the experiments. SPARC is capable of predicting physical−chemical properties at temperatures other than 298.15 K, and UNIFAC can do so, if the vapor pressure is supplied as a function of temperature.

Table SP-2 in the Supporting Information gives the SPARC predictions for the $K_{16OH/A}$ values at 333.15 K, 343.15 K, 353.15 K, 363.15 K, 373.15 K, and 383.15 K. Log $K_{16OH/A}$ prediction from UNIFAC, based on temperature-dependent liquid-state vapor pressure data from the literature[23] are given in Table SP-3. Figure 8 compares these predictions with the measured values

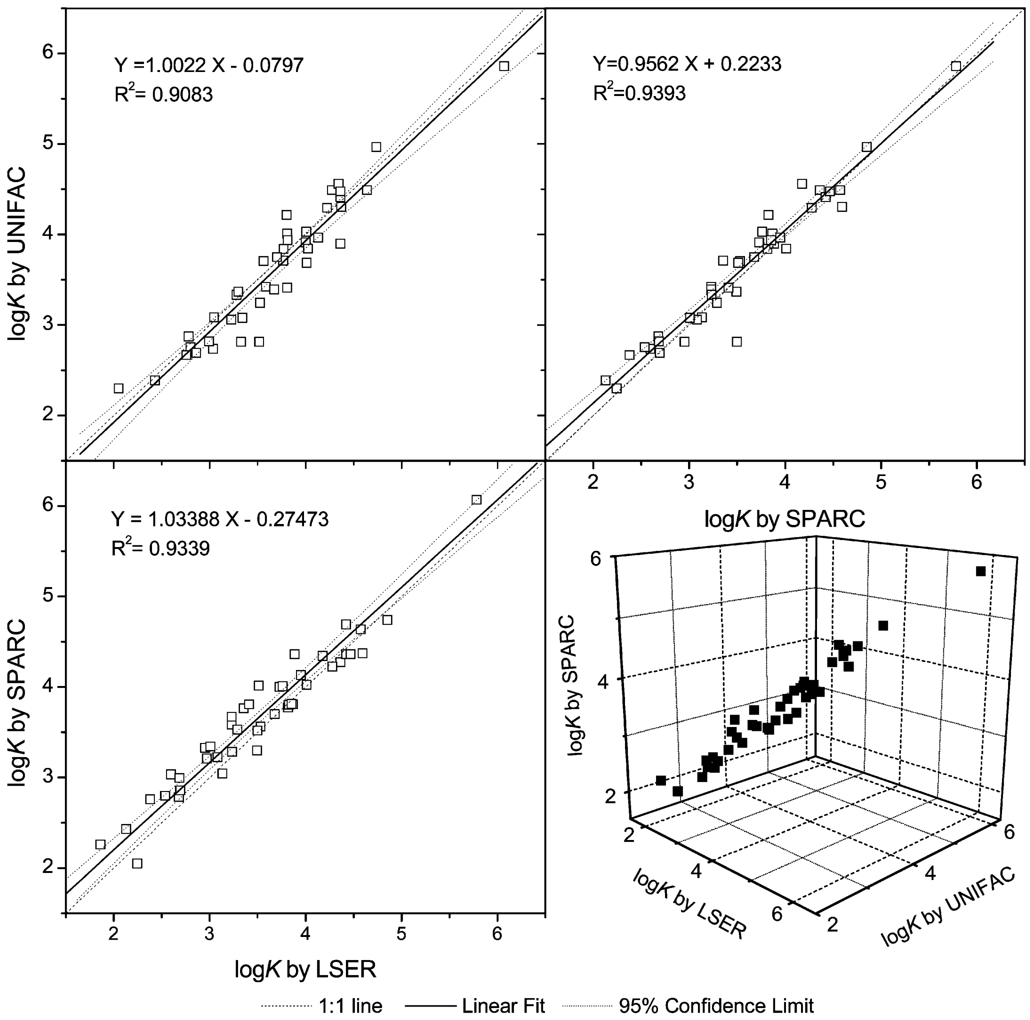

Figure 6. Comparison of the LSER, UNIFAC, and SPARC predictions for the hexadecan-1-ol/air partition coefficient at 298.15 K.

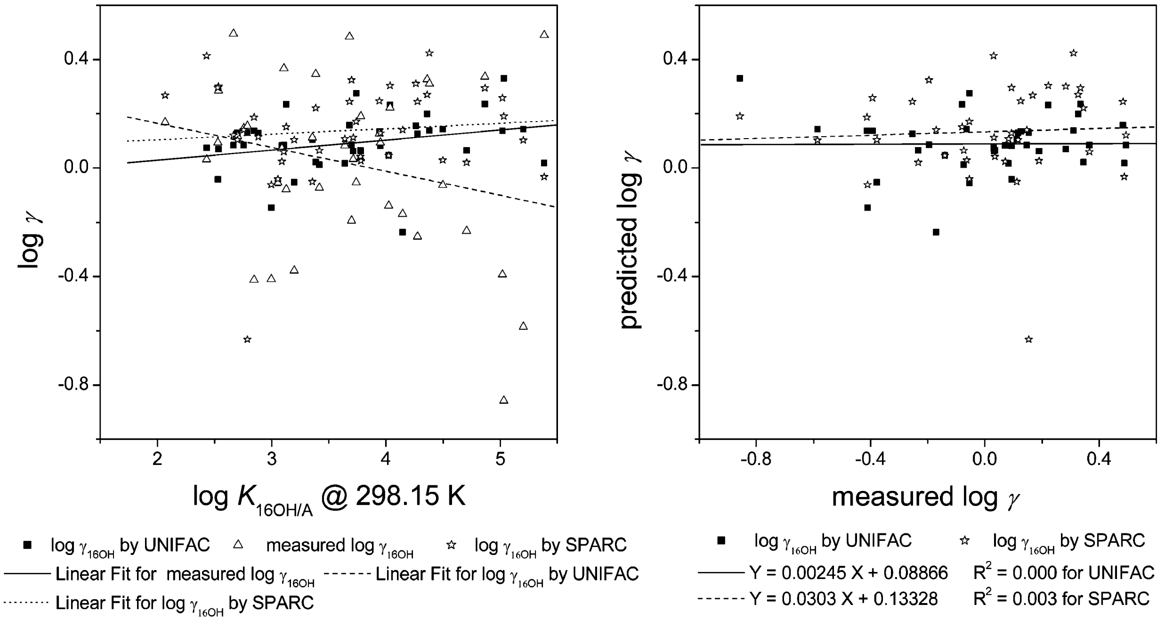

Figure 7. Comparison of experimentally determined activity coefficients in hexadecan-1-ol[8] with UNIFAC predictions.

at the experimental temperature. Both methods estimate partition coefficients that are lower than the measured values, especially for more volatile compounds. At 298.15 K, such trends are not visible, suggesting that both methods probably overestimate the enthalpy of phase transition. In the case of UNIFAC this is simply a result of enthalpies of vaporization $\Delta_{\mathrm{vap}}H$ values that are higher than the measured enthalpies of phase transfer $\Delta_{16\mathrm{OH/A}}H$. Table 6 gives the results of paired samples *t*-tests, which indicates significant difference between either of the two predictions and the measured data. However, the standard

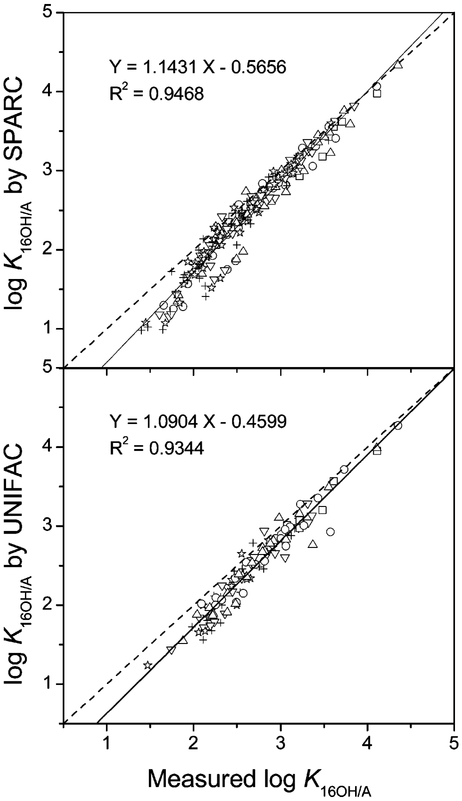

Figure 8. Comparison of experimentally determined hexadecan-1-ol/air partition coefficients at various experimental temperatures:[8] ▽, 333.15 K; ☆, 343.15 K; +, 353.15 K; □, 363.15 K; ○, 373.15 K; △, 383.15 K with the predictions from UNIFAC and SPARC.

deviation and standard error of the mean are small. Considering the experimental uncertainty, which is about 0.5 logarithmic units, such small differences should not be overinterpreted.

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We are grateful to J. M. Prausnitz for providing references on the UNIFAC method.

Supporting Information Available:

Three tables showing LSERs solute descriptors, SPARC predications for log $K_{16OH/A}$, and subcooled liquid−vapor pressure data. This material is available free of charge via the Internet at http://pubs.acs.org.

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