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Henry's Law Constants for Fragrance and Organic Solvent Compounds in Aqueous Industrial Surfactants

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Henry's law constants (k_H) were measured (at 30 °C) and modeled for a suite of fragrance and solvent compounds in aqueous solutions of three structurally diverse industrial surfactants: sodium dodecylbenzene sulfonate (NaDBS), tetradecylbenzyldimethyl ammonium chloride (TDBAC), and a linear alkyl ethoxylate, Neodol 1,9. k_H values for limonene, β-pinene, toluene, and trichloroethene were examined as a function of surfactant concentration. When compared to TCE and toluene, the fragrances limonene and β-pinene with their larger values of molecular polarizability ($\alpha_{mol} = (17.94 \pm 0.5)$ Å^{3}and (17.34 ± 0.5) Å^3, respectively) and greater hydrophobic character exhibited greater affinity for micelles of the linear alkyl ethoxylate relative to those of NaDBS and TDBAC and greater selectivity overall in their interaction(s) with micelles of varying carbon content (C_n). Using a linear solvation energy relationship (LSER) of the form $\ln k_H = C + s\pi_2^* + a\Sigma\alpha_2 + b\Sigma\beta_2$ (π_2^* = solute dipolarity/polarizability; $\Sigma\alpha_2$ = overall solute hydrogen-bond-donor acidity; $\Sigma\beta_2$ = overall solute hydrogen-bond-acceptor basicity; C = a regression constant) as an additional correlation and characterization tool, we find the large negative coefficients on π_2^*, $\Sigma\alpha_2$, and $\Sigma\beta_2$ consistent with the inverse correlation between $\ln k_H$ and the magnitude of solute–solvent interactions in the condensed phase; C decreases with increasing size of the micellar phase. The dominance of HBD and HBA interactions ($\Sigma\alpha_2$ and $\Sigma\beta_2$, respectively) in the LSER for the alkyl ethoxylate points to the role of the ethylene oxide outer portion of the Neodol 1,9 micelles along with the effect of intercalated water.

Introduction

Industrial cleaning formulations contribute to the contamination of indoor environments where occupants are exposed to the volatile and semivolatile organic compounds (VOCs and SVOCs) in surface films and standing solutions of these materials. The commercial products contain numerous chemicals including an aqueous surfactant matrix with added components such as strong bases, chelating agents, solvents, volatile oils, and fragrances.[1] Some of the volatile species in these mixtures have been linked to health outcomes such as asthma and neurotoxicity.[2,3] Some examples of VOCs and SVOCs that occur in water-based cleaners and which are of special concern from a health and exposure standpoint are pinenes, terpenes, and ethers.[1,4] In this work, values of the Henry's law constant (k_H) are determined for selected fragrance and solvent compounds in surfactant dispersions typical of hard surface cleaner formulations. Correlations that relate k_H to surfactant concentration and to solute and surfactant characteristics are explored. A graphical illustration of the partition behavior of VOCs and SVOCs in aqueous surfactant systems is shown in Figure SI-1 of the Supporting Information.

Previous investigations of the apparent k_H for VOCs in solutions of varying surfactant concentration have focused mostly on chlorinated hydrocarbons, especially those of significance to groundwater pollution and surfactant-enhanced remediation.[5–7] However, the VOC/SVOC−surfactant system is also relevant to indoor air quality in which solutes of a much wider range of structure, properties, and corresponding k_H occur. An additional contrast with the groundwater remediation system is that the emphasis (for the outdoor system) is on maximizing pollutant uptake;[6,7] thus, the model surfactant system is often infused with solute(s) at concentrations much higher[6,7] than the infinitely dilute system for which k_H has been traditionally defined.[8] Conversely, fragrances in indoor cleaning solutions can occur at lower or trace concentrations so that their solvation environments may be examined and structure−solvation models may be used to characterize the system, an approach that has not been previously applied in this context.

In this work, we employ k_H to examine the behavior of selected fragrance chemicals with a comparison to that of small chlorinated molecules such as trichloroethene (TCE) and toluene[5] but with a focus on comparing structure and solvation. All k_H values are determined using solute concentrations that are as close as possible to an infinite dilution condition. We take a two-part approach in the analysis and correlation of experimentally obtained k_H for selected fragrance and solvent compounds in individual solutions of three common industrial surfactants (Table 1), sodium dodecylbenzenesulfonate (NaDBS), tetradecylbenzyl dimethyl ammonium chloride (TDBAC), and a linear alkylethoxylate mixture (Neodol 1,9): (1) an analysis of k_H for four solutes, limonene, β-pinene, TCE, and toluene, as function of surfactant concentration for NaDBS, TDBAC, and Neodol 1,9, and (2) use of a revised version of the Abraham linear solvation energy relationship (LSER)[9–11] (eq 1) as a complementary tool for examining solute–solvent processes from the viewpoint of the solvent medium, i.e., the dominant medium effect(s) as expressed by the sign and magnitude of the coefficients a, b, and s on the LSER. In this work, LSERs of the form in eq 1 are created for each of the three micellar

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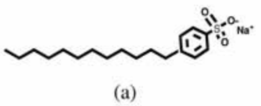
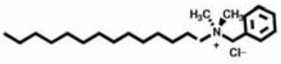
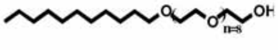
Table 1. Molecular Formulas and Values (or Range) of the CMC (from the Literature) and Concentration Ranges (mol·L^{-1}) Employed for Three Surfactants[1] Used to Create Model Solution Matrices of Hard Surface Cleaners

Surfactant structure	Molecular Formula	CMC (mol L^{-1})	Range (mol L^{-1})
 (a)	$C_{18}H_{29}NaO_3S$	0.00112- 0.0015	0.00 - 0.020
 (b)	$C_{23}H_{42}ClN$	0.0019	0.00 - 0.020
 (c)	C_nH_{2n+1} O- $(C_2H_4O)_m$-H n=11; m=9	N/A[2]	0.00 - 0.05

[1] Surfactants were selected from a water-based cleaner database obtained through the National Toxicology program (NTP), 2001. [2] For the purpose of making a solution *above* the CMC, a (CMC) value of 0.1 mmol·L^{-1} was approximated based on values reported for linear alkyl ethoxylates of similar molecular formula, e.g., $C_nH_{2n+1}O-(C_2H_4O)_m-H$ but with $n = 12$, $m = 9$ (CMC = 0.1 mmol·L^{-1}). The $C_nH_{2n+1}O-(C_2H_4O)_m-H$ linear alkyl ethoxylate with $n = 11$ and $m = 8$ has a reported CMC of 0.299 mmol·L^{-1}. Neodol nonionic surfactants consist of a reaction product mixture that is predominately a C_nH_{2n+1} $O-(C_2H_4O)_m-H$ alkylethoxylate with 8 or 9 ethoxy groups and a C_n corresponding to the number of carbons on the reacting primary alcohol.

systems, NaDBS, TDBAC, and Neodol 1,9, and for pure water as a control using the 14 solutes in Table 2.

$$\ln k_H = C + s\pi_2^* + a\Sigma\alpha_2 + b\Sigma\beta_2 \tag{1}$$

where k_H = the experimentally measured Henry's Law constant ($k_H = C_g/C_{soln}$);[8] π_2^* = solute dipolarity/polarizability parameter; $\Sigma\alpha_2$ = overall solute hydrogen-bond-donor (HBD) acidity; $\Sigma\beta_2$ = overall solute hydrogen-bond-acceptor (HBA) basicity; C = regression constant; and s, a, and b are coefficients of the fitting process.

Experimental

Reagents. D-Limonene, β-pinene, 1,4-cineole, decanal, methanol, 2-propanol, dichloromethane, trichloroethene (TCE), 2-butanone, butyl acetate, and cyclohexane were purchased from Sigma Aldrich. Geranyl nitrile was obtained from TCI. Toluene was obtained from Burdick & Jackson. Ethyl ether and carbon disulfide, the latter used in the preparation of gas-phase standards, were obtained from EM Science. All reagents were of a purity > 95 % and were used as received. Sodium dodecylbenzenesulfonate (NaDBS) and tetradecyl benzyldimethylammonium chloride (TDBAC) were purchased from ICN Biomedical, Inc. Neodol 1,9 (linear alkylethoxylate) was obtained from Stepan Co. These surfactants, selected from three classes (anionic, cationic, and nonionic), were identified as being most prevalent in water-based cleaners. Parameters such as the critical micelle concentration (CMC) and the concentration ranges that were employed are listed in Table 1.

Instrumentation. All headspace (gas phase) measurements were made via a gastight syringe with analysis performed on a Hewlett-Packard (HP) model 6890 GC equipped with a 30 m × 0.32 mm I.D. SPB1 (5.0 μm) fused silica column, a flame ionization detector (FID), and a COMBI-PAL (LEAP Technologies) headspace autosampler. Instrument control and data acquisition were accomplished using Chemstation software.

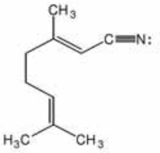
k_H Determination. k_H values were measured by means of bulk equilibration techniques including: (1) the method of equilibrium partitioning in closed systems (EPICS),[12] and (2) a direct phase analysis (DPA) approach involving gas-phase analyte determination coupled with a mass balance approximation of the liquid phase concentration. All values of experimentally determined k_H are reported in dimensionless units with accompanying values of relative standard deviation (RSD) as $S_d/\bar{x}$, i.e., S_d normalized to the mean ($\bar{x}$) and given as (± RSD). Note that values of the un-normalized S_d used in the discussion are given in the text as ± S_d without parentheses. Solute concentrations ranged overall from 0.2 mg·L^{-1} to 94 mg·L^{-1} and were selected based on individual compound solubilities and their limits of detection via a headspace FID signal. For DPA, the range of concentrations for the standards was estimated using literature values of k_H for the VOC/SVOC in question and then further refined based on the actual detector signal obtained from the headspace over a dilute aqueous solution. All headspace signal values were above the limit of detection and were within a precision (± RSD) of < 5 %.

EPICS experiments were conducted by preparing individual spiked samples consisting of either (2 or 12) mL of a solution containing a single VOC. A total of eight spiked samples, four 2 mL and four 12 mL samples, and two blanks containing 2 mL and 12 mL of the solvent were prepared in accordance with EPICS theory.[12] The solutions were contained in sealed 20 mL glass headspace vials and equilibrated at 30 °C for 30 min. The ratio of the headspace concentrations in the 2 mL (headspace = 18 mL) and 12 mL (headspace = 8 mL) vials represented as the ratio of detector response (in area counts) C_{g1}/C_{g2} was used to calculate the dimensionless k_H using eq 2. Three values (in area counts) each of C_{g1} and C_{g2} yielded nine possible combinations of C_{g1}/C_{g2} and nine corresponding values of k_H which were averaged. Values of standard deviation S_d and $S_d/\bar{x}$ (RSD) were calculated from the detector signal based on these replicates.

$$k_H = \frac{(C_{g1}/C_{g2})V_{l1} - V_{l2}}{V_{g2} - (C_{g1}/C_{g2})V_{g1}} \tag{2}$$

where k_H = the dimensionless Henry's law constant; C_{g1} = headspace VOC concentration (area count signal) in vial 1; C_{g2} = headspace VOC concentration (area count signal) in vial 2;

Table 2. 14 Solutes Selected from Compound Groups Common to Commercial Cleaning Products, Additional Species Added for Functional Group Representation in the LSER Training Set, Calculated Solvation Descriptors HBD Acidity $\Sigma\alpha_2$, HBA Basicity $\Sigma\beta_2$, and Dipolarity/Polarizability π_2*[5]

Compound Group	Solute	Description	$\sum\alpha_2$	$\sum\beta_2$	π_2*
Terpene & cyclic alkanes	Limonene 	fragrance (orange)	0.003[1]	0.17[1]	0.53[1]
	β-pinene 	antimicrobial	0.003[1]	0.16[1]	0.29[1]
	cyclohexar		0[3]	0[3]	0.1[3]
Simple alcohols	methanol	solvent	0.43[3]	0.47[3]	0.44[3]
	2-propanol	solvent	0.33	0.56	0.36
Aldehydes	decanal 	fragrance (citrus)	0[1]	0.43[1]	0.63[1]
Halogenated	dichloromethane	solvent	0.1[3]	0.05[3]	0.57[3]
	Trichloroethene[4]	solvent	0.02[3]	0.03[3]	0.65[3]
Aromatic hydrocarbons	Toluene[4]	solvent	0[3]	0.14[3]	0.52[3]
Nitriles	geranyl nitrile 	fragrance (lemon)	0.017[1]	0.28[1]	0.79[1]
Ethers	1,4 cineole 	fragrance (eucalyptus)	0[1]	0.42[1]	0.44[1]
	ethyl ether[2]		0[2,3]	0.45[2,3]	0.25[2,3]
Ketones	2-butanone[2]		0[2,3]	0.43[2,3]	0.61[2,3]
Esters	butylacetate[2]		0[2,3]	0.44[2,3]	0.57[2,3]

[1] Calculated via *Sirius Absolv*.[14] [2] Compound added for LSER. [3] Calculated via *Sirius Absolv* and confirmed by the literature[10] (Abraham, M. H.; Andronian-Haftan, J.; Whiting, G.; Leo, A. *J. Chem. Soc., Perkin Trans. 2* **1994**, 1777−1791). [4] These compounds were found on cleaner formulation MSDS databases. Their role in the formulation is not given. [5] Structures are shown for the fragrances.

V_{l1} = liquid phase volume in vial 1; V_{l2} = liquid phase volume in vial 2; V_{g1} = headspace (gas phase) volume in vial 1; and V_{g2} = headspace (gas phase) volume in vial 2.

DPA experiments, applied to the measurement of k_H for methanol and 2-propanol in pure water and surfactant solutions, were conducted by preparing 10 mL samples consisting of a spiked solution in the 20 mL sealed headspace vials. Equilibrium headspace concentrations were determined from gas-phase calibration standards that were prepared by spiking 5 μL of a liquid phase standard prepared in CS_2 into a 20 mL sealed headspace vial. The method of least-squares was used to produce a linear relationship between known gas phase concentrations and detector response which was applied to the determination of the equilibrium concentration of VOC or SVOC in the headspace. The corresponding liquid-phase concentrations were estimated by mass balance. Equation 3 encompasses both determinations in a single calculation.

$$k_H = \frac{C_g V_l}{C_l V_l - C_g(V_t - V_l)} \tag{3}$$

where k_H = the dimensionless Henry's law constant; C_g = headspace VOC concentration; V_l = liquid volume in the vial; C_l = initial liquid concentration; and V_t = total vial volume.

Parameter Estimation and LSER Preparation. Values of molecular polarizability ($\tilde{\alpha}_{mol}$) used to aid our discussion of solute structure in relation to solute−micelle interactions were calculated after the methods of Miller[13] using ChemSketch. Values are reported in units of Å^3 with an absolute uncertainty given as ± Å^3. Molecular descriptors π_2*, $\Sigma\alpha_2$, and $\Sigma\beta_2$ used in the preparation of LSER equations were calculated using Sirius Absolv PC-based software[14] or obtained from the literature.[9–11] Four individual LSERs were prepared from values of experimental k_H using 14 solutes (Table 2) via multiple linear regression using Microcal Origin version 6 and SAS version 8.1. The solutes were selected from databases of compounds that comprise the fragrance and other components of cleaner formulations (see Table 2). Cyclohexane, diethyl ether, and 2-butanone were added to the solute set to broaden the range of k_H and ensure that all functional groups were represented.

A major challenge in creating LSERs based on k_H lies in their experimental determination over the wide range of values that are characteristic of different classes of organic compounds,

Table 3. Organic Compounds and Fragrances and Their Compound Classes, Values of k_H Measured in Pure Water at 30 °C (This Work), and Comparison with Previously Reported Values at (25 and 30) °C

compd group	compd	description	k_H (RSD)[1] (this work)	k_H (lit.) at 25; at 30 °C	method & reference
terpenes & cyclic alkanes	D-limonene	fragrance (orange scent)	1.57 (± 0.092)	1.304[5]	vp/s[2]
	β-pinene	antimicrobial	2.54 (± 0.118)	6.58[6]	modeled[3]
	cyclohexane	compound added for LSER	5.07 (± 0.0702)	6.13,[7] 9.12	exptl[4]
simple alcohols	methanol	solvent	0.00052 (± 0.017)	$1.86 \cdot 10^{-4}$[8]	exptl[4]
				$1.48 \cdot 10^{-4}$[6]	modeled[4]
	2-propanol	solvent	0.00059 (± 0.018)	$3.31 \cdot 10^{-4}$[5]	exptl[4]
				$4.68 \cdot 10^{-4}$[6]	modeled[3]
aldehydes	decanal	fragrance (citrus)	0.094 (± 0.037)	0.067[9]	exptl[4]
halogenated compounds	trichloroethene	solvent	0.429 (± 0.028)	0.314–0.545;[10] 0.523[14]	exptl[4]
	dichloromethane	solvent	0.128 (± 0.040)	0.092–0.133;[11] 0.147[14]	exptl[4]
aromatic hydrocarbons	toluene	solvent	0.281 (± 0.029)	0.227–0.314;[12] 0.330[14]	exptl[4]
nitriles	geranyl nitrile	fragrance (synthetic lemon)	0.014 (± 0.51)	0.0126[6]	modeled[3]
ethers	1,4-cineole	fragrance (eucalyptus)	0.0104 (± 0.096)	0.0736[5]	vp/s[2]
				0.0043[2]	vp/s[2]
	ethyl ether	compound added for LSER	0.00425 (± 0.005)	0.051–0.053[13]	exptl[4]
esters	butyl acetate	compound added for LSER	0.0193 (± 0.0126)	0.014[13]	vp/s[2]
				0.012, 0.0194[13]	exptl[4]
ketones	2-butanone	compound added for LSER	0.00425 (± 0.005)	0.0053;[14,15] 0.0045[14]	exptl[4]

[1] RSD = relative standard deviation. [2] vp/s = vapor pressure/water solubility (parameter estimation method). [3] "Modeled" implies use of a mathematical parameter estimation method. [4] Value was determined experimentally in the laboratory. [5] Ref 14. [6] Refs 15 and 16. [7] Ref 17. [8] Ref 18. [9] Ref 19. [10] Refs 12 and 20 to 22. [11] Refs 12, 20, 21, 23, and 24. [12] Refs 25 to 27, 20, and 21. [13] Ref 25. [14] Ref 26. [15] Ref 28.

Table 4. k_H Dimensionless (± RSD) for Limonene, TCE, Toluene, and β-Pinene in Aqueous Surfactant Systems and Corresponding NaDBS and TDBAC Solution Concentrations ($\text{mol} \cdot \text{L}^{-1}$)[4]

surfactantconc	limonene		TCE		toluene		β-pinene	
($\text{mol} \cdot \text{L}^{-1}$)	NaDBS	TDBAC	NaDBS	TDBAC	NaDBS	TDBAC	NaDBS	TDBAC
0	1.57 (± 0.092)	1.57 (± 0.092)	0.429 (± 0.028)	0.429 (± 0.028)	0.281 (± 0.029)	0.281 (± 0.029)	2.54 (± 0.12)	2.54 (± 0.118)
0.001[1]	1.54 (± 0.12)	1.20 (± 0.19)						
0.002[1]	1.70 (± 0.038)	0.994 (± 0.23)						
0.005	0.771 (± 0.032)	0.170 (± 0.037)						
0.01[2,3]	0.146 (± 0.037)	0.0348 (± 0.17)	0.359 (± 0.027)	0.286 (± 0.057)	0.227 (± 0.018)	0.163 (± 0.021)	0.354 (± 0.075)	0.200 (± 0.017)
0.015	0.0672 (± 0.12)							
0.02	0.00498 (± 0.32)	0.0275 (± 0.25)	0.320 (± 0.027)	0.219 (± 0.025)	0.179 (± 0.008)	0.117 (± 0.030)	0.0623 (± 0.056)	0.0866 (± 0.059)
0.05			0.177 (± 0.017)	0.110 (± 0.032)	0.0969 (± 0.033)	0.0635 (± 0.040)	0.0277 (± 0.063)	0.0349 (± 0.068)
0.1			0.112 (± 0.041)	0.0689 (± 0.021)	0.0540 (± 0.029)	0.0320 (± 0.029)	0.00340 (± 0.58)	0.0180 (± 0.065)

[1] ≤ the CMC for NaDBS and TDBAC. [2] NaDBS: butylacetate, $k_H = 0.0157$ (± 0.009); 1,4-cineole, $k_H = 0.006$ (± 0.23); decanal, $k_H = 0.053$ (± 0.099); cyclohexane, $k_H = 2.49$ (± 0.104); ethyl ether, $k_H = 0.0598$ (± 0.031); 2-butanone, $k_H = 0.00413$ (± 0.006); dichloromethane, $k_H = 0.116$ (± 0.014); methanol, $k_H = 0.00052$ (± 0.018); 2-propanol, $k_H = 0.00058$ (± 0.017); geranyl nitrile, $k_H = 0.019$ (± 0.24). [3] TDBAC: butylacetate, $k_H = 0.0156$ (± 0.005); 1,4-cineole, $k_H = 0.009$ (± 0.073); decanal, $k_H = 0.063$ (± 0.10); cyclohexane, $k_H = 1.58$ (± 0.107); ethyl ether, $k_H = 0.0539$ (± 0.036); 2-butanone, $k_H = 0.00414$ (± 0.003); dichloromethane, $k_H = 0.102$ (± 0.035); methanol, $k_H = 0.00052$ (± 0.020); 2-propanol, $k_H = 0.00055$ (± 0.010); geranyl nitrile, $k_H = 0.0023$ (± 0.44). [4] k_H for additional compounds in NaDBS and TDBAC systems at 0.01 $\text{mol} \cdot \text{L}^{-1}$, used for the LSER data set, are provided at the base of the table. All measurements performed at 30 °C.

which are necessary to ensure statistical significance of $\Sigma\alpha_2$, π_2^*, and $\Sigma\beta_2$ and to avoid errors in model fitting due to overlap of coefficients. An added complication for aqueous surfactants is the need to select a single surfactant concentration that would be sufficiently high (above the CMC) to promote maximum solute−micelle interactions but not so high that k_H values might be closely clustered or too low for accurate and precise measurement. The surfactant concentrations, 0.01 $\text{mol} \cdot \text{L}^{-1}$ NaDBS and TDBAC and $0.005 \cdot \text{mol L}^{-1}$ for Neodol 1,9, were selected on this premise.

Results and Discussion

Comment on Methods of k_H Determination. Values of k_H measured in this work (Tables 3 to 5)[15–29] ranged from $5.2 \cdot 10^{-4}$ (± 0.018) to 5.07 (± 0.070), a span that necessitated the use of more than one measurement approach. While there are several documented techniques for the determination of k_H, all approaches used here fall into the category of static bulk equilibration methods such as EPICS and other mass balance-based procedures. We recognize that dynamic methodologies, e.g., those based on the purging of solutes from the liquid phase or the continuous movement of liquid and vapor phases against one another,[23] have been preferred for the determination of low k_H (≤0.1). However, systems in which solutes exhibit strong hydrogen bonding to the solvent or which contain surface active agents that foam when the medium is nonstatic might impede the purging process on which these methods are based resulting in considerable measurement error.

Figure 1 illustrates a theoretical calibration curve for the method of EPICs, C_{g1}/C_{g2} vs log k_H computed from eq 2 where $V_{l1} = 2$ and $V_{l2} = 12$, and log k_H and C_{g1}/C_{g2} are varied continuously. The curve shows a region of maximum method sensitivity (point A, Figure 1) corresponding to the range of k_H values for which EPICS has been deemed applicable (0.06 to 0.9).[12,30] However, the regions immediately adjacent to the maximally sloped region (B and C, Figure 1) should be valid, and we have utilized these lower sensitivity portions of the curve to determine k_H for several of the fragrance and alkane species in the solute set (Table 2). For example, our measured mean k_H of 1.57 ± 0.14 and 0.014 ± 0.007 (30 °C) for limonene and the synthetic lemon fragrance geranyl nitrile in pure water, respectively, compare reasonably with estimates based on a ratio of vapor pressure over water solubility: $V_p/\text{sol} = 1.304$[15] and 0.0126[16,17] at 25 °C, respectively. For cyclohexane in pure water, we obtained a dimensionless k_H of 5.07 ± 0.35 which is within the range of several previously reported values for cyclic alkanes

Table 5. k_H Dimensionless (± RSD) for Limonene, TCE, Toluene, and β-Pinene in Neodol 1,9 Aqueous Systems and Corresponding Surfactant Concentrations (mol·L^{-1})[3]

Neodol 1,9 (M)	limonene	TCE	Toluene	β-pinene
0	1.57 (± 0.092)	0.429 (± 0.028)	0.281 (± 0.029)	2.54 (± 0.12)
0.00009[1]	1.41 (± 0.13)			
0.0002[1]	1.58 (± 0.041)			
0.0005	0.797 (± 0.095)			
0.0008	0.505 (± 0.080)			
0.001	0.274 (± 0.030)			
0.005[2]	0.0428 (± 0.12)	0.324 (± 0.020)	0.189 (± 0.020)	0.237 (± 0.038)
0.01		0.260 (± 0.018)	0.161 (± 0.013)	0.105 (± 0.046)
0.02		0.182 (± 0.017)	0.109 (± 0.007)	0.0448 (± 0.023)
0.05		0.0956 (± 0.017)	0.0544 (± 0.037)	0.0190 (± 0.083)

[1] ≤ CMC for Neodol 1,9. [2] Butylacetate, $k_H = 0.0169$ (± 0.01); 1,4-cineole, $k_H = 0.009$ (± 0.10); decanal, $k_H = 0.046$ (± 0.017); cyclohexane, $k_H = 1.92$ (± 0.023); ethyl ether, $k_H = 0.044$ (± 0.065); 2-butanone, $k_H = 0.0041$ (± 0.008); dichloromethane, $k_H = 0.101$ (± 0.053); methanol, $k_H = 0.00053$ (± 0.016); 2-propanol, $k_H = 0.00056$ (± 0.016); geranyl nitrile, $k_H = 0.0188$ (± 0.25). [3] k_H values for additional compounds in Neodol 1,9 at 0.005 mol·L^{-1} used for the LSER data set are provided at the base of the table. All measurements performed at 30 °C.

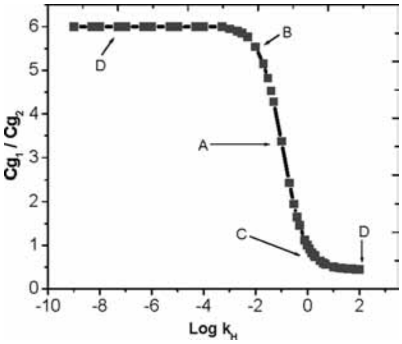


Figure 1. Theoretically generated EPICS calibration plot, C_{g1}/C_{g2} vs log k_H, with plotted values calculated from eq 2, $V_{l1} = 2$ mL, $V_{l2} = 12$ mL, $V_{g1} = 18$ mL, and $V_{g2} = 8$ mL. Points A to D illustrate regions of maximum, minimum, and midrange sensitivity in the measurement of k_H via EPICS for fragrances and compounds in the three solvent systems. A = zone of maximum resolution and sensitivity: the measured k_H for most compounds lie in this region. B = a peripheral region and zone of lower sensitivity corresponding to k_H for limonene and β-pinene measured in 0.1 mol·L^{-1} NaDBS. C = peripheral region of lower sensitivity corresponding to k_H for limonene, β-pinene, and cyclohexane measured in pure water. D = zones of diminished sensitivity that cannot be used.

(4.21 to 8.0 at (27.3 to 27.9) °C).[31] Note that there is a temperature dependence to k_H and that van't Hoff plots (log k_H vs 1/T) have demonstrated slight decreases in k_H with decreasing temperature.[31] With respect to the surfactant systems, k_H values for geranyl nitrile (see Tables 4 and 5) in solutions of NaDBS, TDBAC, and Neodol 1,9 are consistent with the behavior and properties of nitrile ligands. The nonbonding electron pair on the nitrogen of C≡N**:** should result in the greatest solute–surfactant interactions for geranyl nitrile in dispersions of TDBAC, where the positively charged amine headgroup on TDBAC and the C≡N**:** group on the solute should be most strongly attracted, and this is observed. Accordingly, the mean k_H of 0.0023 ± 0.001 for geranyl nitrile in the TDBAC system is an order of magnitude lower than those measured for the NaDBS (0.01 mol·L^{-1}) or Neodol 1,9 (0.005 mol·L^{-1}) ($k_H = 0.019 \pm 0.004$ for 0.01 mol·L^{-1}NaDBS; $k_H = 0.0188 \pm 0.004$ for 0.005 mol·L^{-1} Neodol 1,9; $k_H = 0.0023 \pm 0.001$ for 0.01 mol·L^{-1} TDBAC).

We note that the peripheral regions identified on the curve (B and C) are narrowly defined, and there is a precipitous drop in sensitivity in the measurement of k_H beyond those regions (especially on the low k_H side) marked by an inability to maintain experimental precision within the narrow constraints of the values on the plot (e.g., log k_H in the range of 10^{-4} to 10^{-8}, point D, Figure 1). For the HBD solutes 2-propanol and methanol ($k_H \cong 10^{-4}$), the direct headspace analysis approach became preferable, yielding values of 0.00052 ± 0.000008 and 0.00059 ± 0.00001 for methanol and 2-propanol, respectively, in pure water which are consistent with literature values (Table 3).[16,17,19] The lack of decrease in k_H for these alcohols in the surfactant solutions reflects the small solute size, strong polarity, and HBD character of these solutes which would be expected to lie in the very outer regions of the aqueous solvated micelles.

k_H vs Surfactant Concentration. Of the 14 solutes in Table 2, we selected limonene, β-pinene, TCE, and toluene for the examination of k_H over a range of surfactant concentrations (C_{surf}) primarily above the CMC for each of the three surfactants, NaDBS, TDBAC and Neodol 1,9.[32] These plots are shown in Figures 2 and 3. Note that the *relative* uncertainty increases with decreasing k_H, and this can be attributed to the gradual decrease in headspace analyte signal and corresponding increase in signal-to noise ratio. Included in the plots are values of solute k_H for solutions whose surfactant concentrations were below the CMC. It has been shown in previous studies that there is no effect on solute k_H apart from that of pure water for small chlorinated hydrocarbon solutes in other surfactant systems below the CMC,[5,6] and those observations have been confirmed here for the four solutes. Where a goal of this work has been to observe relationships among surfactant properties and k_H to see if there can be a basis for predictive modeling, we have fitted the k_H vs C_{surf} plots with a first-order exponential decay function and used the individual trends, in $\Delta k_H/\Delta C_{surf}$ specifically the region of maximum decrease in k_H, as a basis for making structural and mechanistic inferences.

The best fit first-order decay for limonene, β-pinene, TCE, and toluene for each of NaDBS, TDBAC, and Neodol 1,9 illustrates, overall, that the number of carbons on the surfactant molecules is proportional to the initial magnitude of $\Delta k_H/\Delta C_{surf}$ *beyond* the CMC. The hydrocarbon content for the three surfactants is highest for Neodol 1,9 (C_{29}), lowest for NaDBS (C_{18}), and midrange for TDBAC (C_{23}). Note that the very large k_H for β-pinene in pure water ($k_H = 2.54 \pm 0.304$) makes the plotted trend less noticeable where the pure water data are included (Figure 2b). The first-order decay fitting of a narrower range of k_H (inset graph, Figure 2b) better illustrates the structural relationship as described. The observed trend, i.e., the increase in $\Delta k_H/\Delta C_{surf}$, with increasing surfactant carbon content, appears most pronounced for the two largest and most polarizable solutes, limonene and β-pinene. Values of polarizability (α_{mol}) were calculated at (17.94 ± 0.5) Å^3 and (17.34 ± 0.5) Å^3, respectively; note that our calculated α_{mol} for toluene [(12.32 ± 0.5) Å] and TCE [(10.21 ± 0.5) Å^3] match those of the published data.[33] These observations are consistent with early studies of vapor solubility in which inverse trends between ln

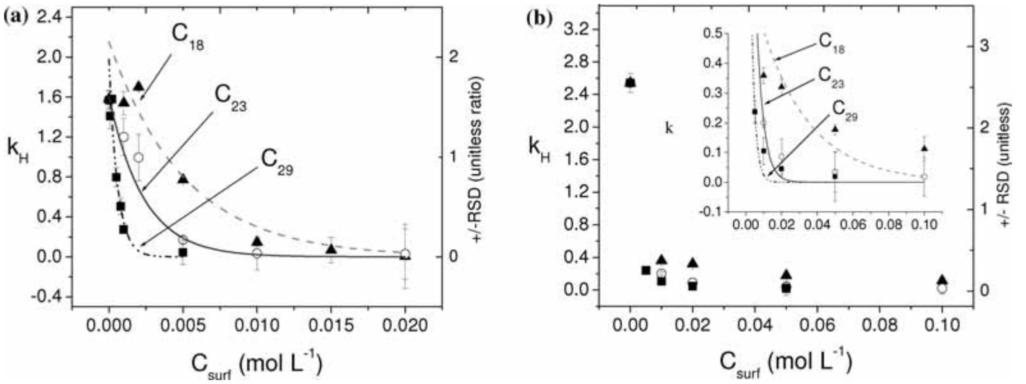


Figure 2. k_H (dimensionless) uncertainty as (± RSD) on 2nd *y*-axis, for limonene (a) and β-pinene (b) vs concentration of surfactant: NaDBS (▲, dashed line; CMC = (0.00112 to 0.0015) mol·L^{-1}), TDBAC (○, solid line; CMC = 0.0019 mol·L^{-1}), and Neodol 1,9 (■, dash and dot; CMC ~ 0.0001 mol·L^{-1}, see Table 1). Fitted curves are first-order decay.

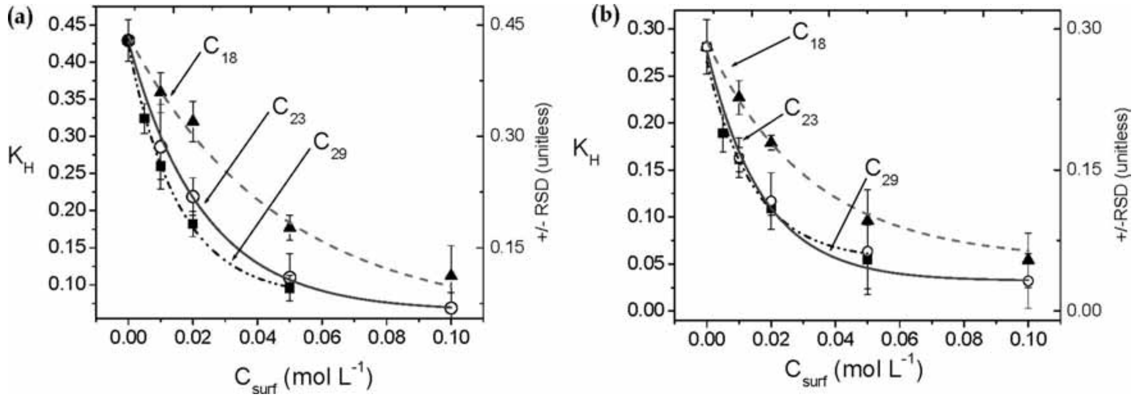


Figure 3. k_H (dimensionless) uncertainty as (± RSD) on 2nd *y*-axis, for TCE (a) and toluene (b) vs concentration of surfactant: NaDBS (▲, dashed line; CMC = (0.00112 to 0.0015) mol·L^{-1}), TDBAC (○, solid line; CMC = 0.0019 mol·L^{-1}), and Neodol 1,9 (■, dash and dot; CMC ~ 0.0001 mol·L^{-1}, see Table 1). Fitted curves are first-order decay.

k_H and solute polarizability were observed for solutes in several organic solvent media.[34] Unlike TCE and toluene which are smaller, more dipolar, and can engage in a wider variety of noncovalent interactions *in addition* to the "hydrophobic effect",[35] interactions of limonene and β-pinene, with their more "alkane-like" structure with micelles of the three surfactants, should reflect the hydrophobic effect almost entirely, and hence we see the more clear trend in $\Delta k_H/\Delta C_{surf}$ with surfactant carbon content (C_n) for these structures (Figures 2a,b). The particularly strong interactions of β-pinene and limonene with micelles of the alkyl ethoxylate (Neodol 1,9) may be further explained by considering the nature of Neodol 1,9 aggregates. For example, previous theoretical and NMR studies of micelles of nonionic surfactants[36] suggest that such aggregates possess a hydrophobic core comprised of the alkane component of the surfactant molecule along with an outer more flexible portion where waters of hydration penetrate between the (outer) ethylene oxide chains[36] (Table 1c). The strong attraction of "hydrocarbon-like" solutes (β-pinene and limonene) for the hydrophobic core may involve the expulsion of adsorbed water molecules (from the outer flexible region of the aggregate) making the overall free energy of solute transfer *more* favorable as it may involve a more favorable entropic contribution.[35]

Unlike the fragrances (limonene and β-pinene), toluene and TCE which are smaller and more polar exhibit slightly different trends in $\Delta k_H/\Delta C_{surf}$ for the three surfactants (Figures 3a–b). For these solutes, the magnitude of $\Delta k_H/\Delta C_{surf}$ in the maximum sloped region is more similar for TDBAC (C_{23}) and Neodol 1,9 (C_{29}) suggesting that factors besides surfactant C_n play a role in solute sorption and partitioning. While Neodol 1,9 (Table 1c) consists solely of linear alkyl and alkyloxy moieties, micelles of TDBAC (Table 1b) possess an outer headgroup region that is aromatic *and* cationic, thus enabling conjugated and aromatic solutes to engage in π-π[37,38] and π-cation interactions[39,40] in addition to the dispersion forces between nonconjugated alkyl components. The greater range of weak forces that encompass aromatic interactions enables the C_{23} surfactant to compete effectively for *these* solutes (i.e., relative to the C_{29} surfactant).

Table 6. Probability Values (*prob* > *t*)[1] for Coefficients of the Variables $\Sigma\alpha_2$, $\Sigma\beta_2$, π_2*, and the Intercept for LSERs in Equations 4 to 7

eq no.	*y*-intercept	$\Sigma\alpha_2$	$\Sigma\beta_2$	π_2*
4	0.019	0.003	$4.1\cdot10^{-4}$	0.024
5	0.082	$8.01\cdot10^{-4}$	<0.0001	0.0174
6	omitted	0.008	0.001	0.0104
7	0.047	0.002	<0.0001	omitted

[1] The probabilty that the null hypothesis is true, in terms of a T statistic.

Analysis of LSER Results. The fitted LSERs for pure water and the three micellar systems (0.01 mol·L^{-1} NADBS, 0.01 mol·L^{-1} TDBAC, and 0.005 mol·L^{-1} Neodol 1,9),[41] respectively, are listed below in eqs 4 to 7. Values of observed significance (probability as $p > t$) for each variable in the individual equations, e.g., $\Sigma\alpha_2$, $\Sigma\beta_2$, π_2*, and *C* are given in Table 6.

$$\ln k_H = (2.71 \pm 0.98) - (9.55 \pm 2.52)\Sigma\alpha_2 - (9.36 \pm 1.80)\Sigma\beta_2 - (4.59 \pm 1.73)\pi_{2*} \quad \left(N = 14;\ S_d = 0.84;\ r^2 = 0.883\right) \tag{4}$$

$$\ln k_{\mathrm{H}} = (1.28 \pm 0.66) - (8.11 \pm 1.71)\Sigma\alpha_2 - (8.53 \pm 1.22)\Sigma\beta_2 - (3.36 \pm 1.18)\pi_{2*}$$
$$(N = 14;\ S_{\mathrm{d}} = 0.76;\ r^2 = 0.926) \qquad (5)$$

$$\ln k_{\mathrm{H}} = (-7.55 \pm 2.33)\Sigma\alpha_2 - (6.69 \pm 1.56)\Sigma\beta_2 - (2.86 \pm 0.92)\pi_{2*}$$
$$(N = 14;\ S_{\mathrm{d}} = 1.05;\ r^2 = 0.9542) \qquad (6)$$

$$\ln k_{\mathrm{H}} = (-0.88 \pm 0.39) - (7.14 \pm 1.76)\Sigma\alpha_2 - (7.59 \pm 1.27)\Sigma\beta_2$$
$$(N = 14;\ S_{\mathrm{d}} = 0.79;\ r^2 = 0.866) \qquad (7)$$

All listed p values (Table 6) are < 0.05, indicating significance at the 95 % probability level, with the exception of the intercept C in eq 5 for which p is 0.082 (significance at 92 % probability). Values of standard deviation (as $\pm\ S_{\mathrm{d}}$) for the coefficients a, b, and s (eqs 4 to 7) are comparable in relative magnitude to those obtained by previous researchers for LSERs describing other interfacial sorption and partitioning processes.[42] The overall fit expressed as the coefficient of determination (r^2) ranged from 0.883 and 0.866 for the pure water and Neodol 1,9, respectively, to 0.9542 for the TDBAC system. These values reflect the fact that we have included compounds with environmental and pharmacological significance in the calibration set (Table 2) rather than utilizing only the standard small molecules that are more typically, though not exclusively,[43] applied in LSER studies.[44,45] Structural differences among these more complex species (e.g., limonene, β-pinene, geranyl nitrile, 1,4-cineole) are not always reflected in their bulk phase partitioning behavior, and this may be due to the fact that critical functionality are embedded in a more bulky solute structure and thus specific solute–solvent interactions are less well reflected in the coefficients leading to poorer fits and higher coefficient error. When we replace the fragrances with the standard small molecules that are traditionally used in LSERs for k_{H} (e.g., propane, hexane, and benzene),[45] the model for pure water produces an r^2 of 0.967 ($n = 17$). Plots of ln k_{H} predicted via LSER vs ln k_{H} from experimental measurement are given in Figure 4 for the three micellar systems.

Given enough fitting parameters, the Abraham solvation models (e.g., eq 1) can become independent of the solute set, i.e., in terms of the magnitude of the fitting coefficients (e.g., a, b, s). But that has not been achieved here, and likely this is due to the nature and size of the solute set and system complexity. Equation 4 (for pure water), however, is in good agreement with another recent pure solvent model based on log $C_{\mathrm{S}}/C_{\mathrm{g}}$ where C_{S} is the liquid phase solute molar solubility and C_{g} is the corresponding solute saturated vapor phase concentration.[46] The latter model contains the additional parameters log L (logarithm of the solute gas−hexadecane partition coefficient at 298.15 K), V_x (the solute characteristic McGowan volume), and R (solute excess molar refraction), which we did not find valid for our systems.

For the TDBAC system (eq 6), we were able to improve the fit of the variables by eliminating the intercept (i.e., let $C = 0.0$). In the multivariate regression of ln k_{H}, C represents a component of ln k_{H} that is not accounted for by any of the fitted parameters. Previous discussions of C in LSER correlations of ln k' (log of the chromatographic retention factor) for micellar electrokinetic chromatographic (MEKC) systems have suggested that C is proportional to the phase volume ratio $V_{\mathrm{micelle}}/V_{\mathrm{aq}}$ for micelles in the electrophoretic buffer.[47,48] In *this work*, we observe a trend in the magnitude of C with micelle size. Note the size of a micelle is proportional to the length of individual monomers as well as the nature of monomer packing in the aggregate, and these criteria can influence the extent of solute intercalation especially in the context of solute size. For the LSERs in eqs 4 to 7, C ranges from a large positive value (2.71) for pure water to smaller and smaller values (2.71, 1.28, 0.00, and −0.88), respectively, as the solvent transitions from pure water to one containing an increasingly large pseudophase partition media, e.g., water → NaDBS → TDBAC → Neodol 1,9.

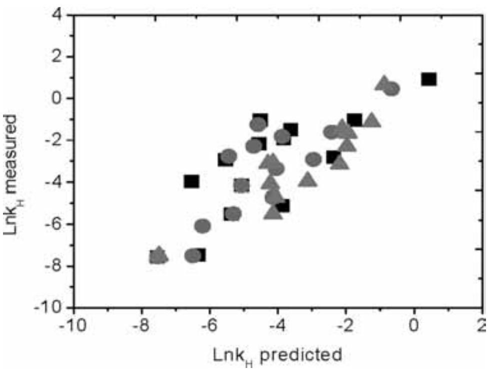


Figure 4. ln k_{H} predicted vs ln k_{H} measured for 14 solutes (Table 2) using LSERs for ■, 0.01 mol·L^{-1} NaDBS (eq 5), ●, 0.01 mol·L^{-1} TDBAC (eq 6), and ▲, 0.005 mol·L^{-1} Neodol 1,9 (eq 7).

The large negative coefficients on all of the solvation descriptors reflect the strong inverse correlation between k_{H} and the magnitude of solute–solvent interactions (i.e., through HBA, HBD, and dipolar effects). That the coefficients (a, b, s) are largest and most negative for pure water (eq 4) is consistent with the assumption that water is the most dipolar and hydrogen bonding component of the solvent system. As micelles are added, the individual analytes become solvated in the outer headgroup region of the aggregates resulting in incremental increases in a, b, and s, i.e., becoming less negative as the analytes partition into the outer portion of the aggregates. In terms of coefficient sign and magnitude, our results are consistent with those of LSER studies describing other interfacial sorption and partitioning processes. For example, in a previously published LSER describing the sorption of small organic solutes from an inert gas to an organobentonite clay,[42] there is a strong positive correlation between ln K_{p} ($K_{\mathrm{p}} = C_{\mathrm{clay}}/C_{\mathrm{gas}}$) and $\Sigma\alpha_2$, π_2*, and $\Sigma\beta_2$, which is consistent with the chemistry of that interfacial process. The lack of solute solvation in the inert gas results in a large net driving force for interaction with the surface organic layer on the clay. In this work, the driving force for an increase in magnitude of k_{H} is toward *decreased* solvation (via HBA, HBD, and dipolar interactions) in the aqueous phase, hence the negative coefficients. In the previously cited MEKC studies[47,48] where LSERs were used to explore micelle containing electrophoretic buffers prepared from surfactants of varying monomer chain length or headgroup composition, ln k' has a much more complex and less direct dependence on solute solvation in the different phases within the buffer, as would be expected. Accordingly, the coefficients a, b, and s (in that work) are smaller in magnitude and sometimes positive or negative.[47,48]

For the Neodol 1,9-based LSER, eq 7, the π_2* parameter was removed due to lack of a statistically valid fit ($p >> 0.05$) for the variable. A rationale consistent with the chemistry of the system is as follows. While the surfactant concentration is well above the CMC for Neodol 1,9 ($C_{\mathrm{surf}} = 0.005$ M), C_{surf} is still not sufficiently high to allow solutes to be deeply partitioned within the organic aggregates. Recall also that these micelles are large loosely packed aggregates, and thus the majority of the compounds, particularly the polar species, should lie among the ethylene oxide chain portion where the medium has both

HBA and HBD character due to the individual oxide groups and the terminal −OH, respectively (Table 1, structure C). Given that water molecules also are intercalated among the outer monomer chains in this portion of the micelle, $\Sigma\alpha_2$ and $\Sigma\beta_2$ become dominant variables in the LSER. Conversely, NaDBS and TDBAC (eqs 5 and 6, respectively) have aromatic groups as part of the outer headgroup region, thus promoting $\pi-\pi$ and aromatic interactions. Thus, π_2* remains a significant parameter in the LSER for those systems (eqs 5 and 6).

In the C_{surf} trend experiments (Figures 2 and 3) where the focus was on the behavior of limonene and β-pinene, we could observe a specific surfactant attribute (C_n) that reflected the properties and partitioning mechanism of *those* solutes, e.g., strong hydrophobic interactions with the Neodol 1,9 micelle and increasing sorption (as $\Delta k_H/\Delta C_{\text{surf}}$) with increasing surfactant hydrocarbon content. In the LSER for Neodol 1,9, we observe a snapshot of a single micellar solvation environment ($C_{\text{surf}} = 0.005\ \text{mol}\cdot\text{L}^{-1}$) from the viewpoint of many solutes which are largely solvated in the more *aqueous* outer ethylene oxide portion (of the micelle). Thus, we observe a polar hydrogen-bonding environment on the part of the aqueous Neodol 1,9 system as opposed to its strong hydrophobic binding properties.

Acknowledgment

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Supporting Information Available:

Figure SI-1. This material is available free of charge via the Internet at http://pubs.acs.org.

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