Estimating Partition Coefficients for Fuel−Water Systems: Developing Linear Solvation Energy Relationships Using Linear Solvent Strength Theory To Handle Mixtures

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In many environmental transport problems, organic solutes partition between immiscible phases that consist of liquid mixtures. To estimate the corresponding partition coefficients, we evaluated the efficacy of combining linear solvation energy relationships (LSERs) developed for pure 1:1 systems via application of linear solvent strength theory. In this way, existing LSERs could be extended to treat solute partitioning from gasoline, diesel fuel, and similar mixtures into contacting aqueous mixtures. Unlike other approaches, this method allowed prediction of liquid−liquid partition coefficients in a variety of fuel−water systems for a broad range of dilute solutes. When applied to 37 polar and nonpolar solutes partitioning between an aqueous mixture and 12 different fuel-like mixtures (many including oxygenates), the root-mean-squared error was a factor of ∼2.5 in the partition coefficient. This was considerably more accurate than application of Raoult's law for the same set of systems. Regulators and scientists could use this method to estimate fuel−water partition coefficients of novel additives in future fuel formulations and thereby provide key inputs for environmental transport assessments of these compounds.

Introduction

The discovery of nationwide contamination of subsurface drinking water sources by methyl *tert*-butyl ether (MTBE) has demonstrated that gasoline constituents can seriously threaten thousands of community water supplies in the U.S. (*1−4*). Subsequent work has scrutinized the danger posed by other less abundant gasoline components, such as phenol and aniline derivatives, that are also polar and relatively water-soluble (*5*, *6*). In the wake of these activities, the need for environmental transport modeling of existing and future fuel constituents has become increasingly apparent (*3*).

Environmental fate assessment of fuel components relies heavily on fuel−water partition coefficient ($K_{i,fw}$) values (*4*, *7*, *6*, *8*), defined as

$$K_{i,fw} = \frac{\text{solute concentration in the fuel phase}}{\text{solute concentration in the aqueous phase}} \quad (1)$$

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for solute i distributed between a fuel (*f*) phase and an aqueous (*w*) phase. More generally, organic contaminant transport modeling requires information on solvation energetics in a wide variety of environmental media. For example, nonionic organic solutes typically have substantially different solvation energies in diverse organic phases such as wood (lignin) (*9*), soil organic matter (*10*), sediment organic matter (*10*), humic acid (*11*), and gasoline (*5*). Conventional approaches to calculating solvation behavior (UNIQUAC (*12*), UNIFAC (*13−15*)) cannot treat mixtures having solute−solvent interactions between a broad range of heteroatomic moieties. Traditional empirical methods (Linear Solvation Energy Relationships (*16*), Linear Free Energy Relationships (*17*), fragment methods (*18−20*)) are usually selective to particular solvent systems and require substantial parameter fitting from existing data. No single approach can estimate solvation energetics of organic contaminants in a wide range of multicomponent environmental mixtures. Until more generalizable solvation theories have been validated, it is useful to draw on a suite of methods, depending on the application.

In the present work, we develop and test an empirical method which is tailored to the challenge of estimating solute partitioning in fuel−water mixtures. This problem does not easily fall into the scope of previous models or estimation methods. Typically, the fuel−water equilibria of hydrocarbons are estimated assuming ideal solution conditions (Raoult's law) in the fuel mixture (*21−27*). However Raoult's law is likely to be inaccurate for polar fuel constituents, since these compounds may experience very different intermolecular interactions in a nonpolar fuel phase than in their pure liquid (ideal) state. Additionally, polar fuel constituents (e.g., phenols and anilines) may be especially sensitive to the presence of other polar additives such as oxygenates. Consequently it is desirable to generate a solvation model for fuels which could be accurately applied to coexisting polar and nonpolar fuel constituents.

Estimation of fuel−water equilibria poses the additional challenge that fuel and oil compositions vary widely by type. Retail and industrial fuel formulations are adjusted regionally and seasonally as well as in response to new regulatory requirements, engine advances, and market influences. Liquid fuels are usually composed of mostly hydrocarbons, but they typically include additives or processing byproducts which contain heteroatoms (i.e., O, N, or S); such compounds may therefore affect the solvation properties of the fuel mixture (*28*, *29*). Conventional (not oxygenated) automotive retail gasolines contain $C_4−C_{12}$ alkanes (45% to 65% by mass), low molecular weight aromatic hydrocarbons (20% to 40% by mass), and low molecular weight olefins (5% to 15% by mass) (*30*). As of this writing, oxygenated gasolines in many regions are required to contain more than 10% MTBE or ethanol by volume, and these regulations are likely to change soon (*31*). Diesel (*32*) and aviation (*33*) fuels generally include higher molecular weight components than gasoline and tend to be enriched in aliphatic compounds relative to gasoline. Motor oils have yet higher average molecular weights (250 to 1000 Daltons), and they contain significant quantities of both aromatic and aliphatic components as well as numerous additives (*25*). Finally, many other liquids of concern are highly variable and unrefined mixtures of large molecular weight hydrocarbon compounds. For instance, coal tar, a waste product of coal gasification, often has substantial levels of oxygen-containing (up to 33% by mass) and sulfur-containing (up to 4% by mass) impurities (*24*, *34*). These examples of organic liquid mixtures have varied compositions, but they all are predominantly made up of hydrocar-

bons and sometimes have significant quantities of polar constituents.

Partitioning Model Theory for Mixtures. Linear Solvation Energy Relationships (LSERs) allow accurate estimation of partition coefficients for a wide range of organic solutes in various solvents and organic mixtures (standard deviation, $\sigma_{\log K, LSER} = 0.10$ to 0.25 ($35-40$)). The general LSER treatment relates a solute's partition coefficient to five independent solvation parameters of that solute and five coefficients specific to a given two-phase system, plus an intercept (c)

$$\log K_{i,pq} = c + rR_2 + s\pi_2^H + a\alpha_2^H + b\beta_2^H + \nu V_x \quad (2)$$

where $K_{i,pq}$ is the partition coefficient of solute i between liquid or gas phases, p and q. The parameters R_2, π_2^H, α_2^H, β_2^H and V_x describe the excess molar refraction (16), polarity/polarizability (41), hydrogen-bonding acidity (42), hydrogen-bonding basicity ($43, 44$), and group-contributable molecular volume (45), respectively, of solute i, and c, r, s, a, b, and ν are adjusted coefficients specific to the two-phase system, $p-q$. A key limitation to using LSERs for assessing fuels is the need for copious partitioning data to calibrate the LSER coefficients for individual fuel-environmental media (e.g., water) combinations.

However, the linear solvent strength approximation (often referred to as the log-linear cosolvency model (46)) may be used to develop a mixing rule for use of LSERs deduced for 1:1 immiscible liquids, thereby allowing straightforward construction of estimated LSERs for novel mixtures. According to linear solvent strength theory (LSST), the solubility of solute i in a mixture phase is given by (47)

$$\log S_{i,p} = \left(1 - \sum_{j\neq w}\phi_j^p\right)\log S_{i,w} + \sum_{j\neq w}\phi_j^p \log S_{i,j} = \\ \sum_j \phi_j^p \log S_{i,j} \quad (3)$$

where $S_{i,p}$ is the solubility of solute i in mixture phase p; $S_{i,w}$ is the solubility of solute i in pure water; $S_{i,j}$ is the solubility of solute i in pure cosolvent j; and ϕ_j^p is the volume fraction of each cosolvent j in mixture p. Equation 3 is formulated with water as a reference solubility (using pure liquid i as the standard state) because LSST has conventionally been used to model organic solutes in aqueous/organic cosolvent mixtures, including applications in drug development (47, 48), reverse phase liquid chromatography (49, 50), and environmental fate modeling (51, 52). LSST is believed to be most applicable to cases in which the mixed solvent is polar (48), making it a simple and powerful approach for extrapolating the solubilities of a wide range of solutes in polar cosolvent-aqueous mixtures ($50, 51, 53$). Li (54) applied LSST to common aqueous/cosolvent binary mixtures for over 1000 solutes and found absolute average discrepancies with observed log S values of ~0.1 to 0.4, depending on the cosolvent. In addition to contrived (laboratory) ternary mixtures, relevant environmental systems such as fuel-water/cosolvent and natural sorbent-water/cosolvent systems have been characterized effectively using LSST. Several workers have used LSST to model the partitioning of polycyclic aromatic hydrocarbon (PAH) compounds in fuel-water or similar systems containing methanol, ethanol, 2-propanol, acetone, acetonitrile, or MTBE cosolvents (22, 27, 46, 54, 55). Fu and Luthy demonstrated that LSST accurately described soil-water/methanol partitioning equilibria of naphthalene, naphthol, quinoline, and 3,5-dichloroaniline (52). Spurlock and Biggar verified LSST application to soil-water partitioning of several phenylurea herbicides in the presence of methanol or dimethyl sulfoxide solvent (56). Lee and co-workers showed that LSST could explain pentachlorophenol equilibria between soils and methanol/

water, acetonitrile/water, and dimethyl sulfoxide/water mixtures; however, LSST failed to fit benzoic acid sorption behaviors under similar conditions ($57-59$). Rao et al. found that sorption of several PAH compounds to soil from methanol/water, dimethyl sulfoxide/water, and several partially miscible organic solvent/water systems could be described accurately by LSST (60). Hayden and co-workers recently showed that LSST could accurately explain tetrachloroethylene partitioning between 2-propanol/water or ethanol/water mixtures and an activated carbon surface (61). Hence, we surmised that LSST provides the basis for a simple mixing rule for LSERs.

To extend LSERs to new 1:1 phase partitioning mixtures, we combined these models. From eq 3, partitioning of solute i between two phases p and q can be described generally as

$$\log K_{i,pq} = \log S_{i,p} - \log S_{i,q} \\ = \sum_j \phi_j^p \log S_{i,j} - \sum_k \phi_k^q \log S_{i,k} \quad (4)$$

Adding and subtracting the log solubility of i in water, $\log S_{i,w}$, to the right-hand-side

$$\log K_{i,pq} = \sum_j \phi_j^p \log\left(\frac{S_{i,j}}{S_{i,w}}\right) - \sum_k \phi_k^q \log\left(\frac{S_{i,k}}{S_{i,w}}\right) \\ = \sum_j \phi_j^p \log(K_{i,jw}) - \sum_k \phi_k^q \log(K_{i,kw}) \quad (5)$$

where $\log K_{i,jw}$ and $\log K_{i,kw}$ are the solvent k-water and solvent j-water partition log coefficients of solute i; and j and k are the solvent components of the mixtures p and q, respectively. It is worth noting that for solvent component k = water, one finds $K_{i,ww} = 1$. Consequently, for the case where phase q is pure water, the corresponding summation in eq 5 vanishes to zero. Employing the LSER formulation (eq 2), the solvent volume-fraction additivity of log K values for mixture components (eq 5) therefore implies that

$$\log K_{i,pq} = \sum_j \phi_j^p \Big(c_{jw} + r_{jw}R_2 + s_{jw}\pi_2^H + a_{jw}\alpha_2^H + \\ b_{jw}\beta_2^H + \nu_{jw}V_x\Big) - \sum_k \phi_k^q \Big(c_{kw} + r_{kw}R_2 + s_{kw}\pi_2^H + \\ a_{kw}\alpha_2^H + b_{kw}\beta_2^H + \nu_{kw}V_x\Big) \quad (6)$$

This equation suggests that the set of system LSER coefficients ([c], [r], [s], ...) may be specified using established pure liquid-liquid LSER coefficients.

Wang et al. (62) applied eq 6 to a set of reverse phase liquid chromatographic systems. They investigated a broad range of solutes partitioning between a stationary saturated C_8 hydrocarbon phase and an aqueous binary phase having an eluent modifier (cosolvent) of methanol, acetonitrile, or tetrahydrofuran. With respect to eq 6, this means that partitioning was between a stationary phase (p) and mixture (q) of water (w) and single organic cosolvent (z). Over a range of mixture compositions (ϕ_2^q), the partition coefficient could be described using

$$\log K_{i,pq} = (c_{pw} + r_{pw}R_2 + s_{pw}\pi_2^H + a_{pw}\alpha_2^H + b_{pw}\beta_2^H + \\ \nu_{pw}V_x) - \phi_z^q(c_{zw} + r_{zw}R_2 + s_{zw}\pi_2^H + a_{zw}\alpha_2^H + b_{zw}\beta_2^H + \\ \nu_{zw}V_x) \quad (7)$$

where the stationary phase was assumed to be pure (component $j = p$) and therefore $\phi_p^p = 1$, and where for solvent component k = water, the term $\phi_w^q \log K_{i,ww} = 0$. These workers fitted so-called "global" LSER coefficients to

TABLE 1. Compositions of Synthetic and Retail Fuel Mixtures

index	mixture type	composition (by volume percent)
1.	synthetic gasoline (*67*)	24% hexane, 32% 2,2,4-trimethylpentane, 3% benzene, 7% toluene, 24% xylenes
2.	synthetic gasoline (*66*)	83.1% 2,2,4-trimethylpentane, 0.8% benzene, 5.8% toluene, 2.6% ethylbenzene, 7.7% xylenes, + variable ethanol amendment
3.	retail gasolines (*5*)	52% aliphatic hydrocarbons, 34% aromatic hydrocarbons, 5.3% olefins, 6.5% methyl *tert*-butyl ether
4.	isooctane−MTBE mix (*5*)	95% isooctane, 5% methyl *tert*-butyl ether
5.	isooctane−MTBE mix (*5*)	85% isooctane, 15% methyl *tert*-butyl ether
6.	isooctane−MTBE mix (*5*)	70% isooctane, 30% methyl *tert*-butyl ether
7.	toluene−MTBE mix (*5*)	95% toluene, 5% methyl *tert*-butyl ether
8.	toluene−MTBE mix (*5*)	85% toluene, 15% methyl *tert*-butyl ether
9.	toluene−MTBE mix (*5*)	70% toluene, 30% methyl *tert*-butyl ether
10.	diesel fuel survey (*32*)	83% aliphatic hydrocarbons, 15.3% aromatic hydrocarbons, 1.4% olefins

all three systems with modifier concentrations of up to 50% by volume. In other words, the set of twelve LSER coefficients of eq 7 were fitted to solute partitioning data which reflected a range of ϕ_z values ($\phi_z = 0.10$ to $\phi_z = 0.50$) for each binary (water plus cosolvent) system. This approach gave calculated solute partitioning free energy values as accurate as results found for LSERs that have been derived for systems of fixed composition ($\sigma_{\log K, Wang} \sim 0.10$), showing that the LSST approximation is very useful for the conditions that Wang et al. considered.

In cases where there are not sufficient data to fit the coefficients of eq 6, one may simply apply known pure-component LSER coefficients and thereby estimate the partitioning properties of solutes in mixtures. We refer to mixture LSERs estimated in this way as "LSST-derived LSERs." In this paper, we evaluate the efficacy of LSST for extending pure phase LSER coefficients to new mixture systems. Fuel mixtures with both nonpolar and polar constituents are used as a set of test cases. It is worth noting a special concern. Previous investigators suggest that LSST applies best to systems in which the solute is less polar than the solution mixture (*48, 63*). However most systems under consideration here contain a nonpolar (fuel) phase in which polar solutes are dissolved into moderately polar or nonpolar mixtures. Therefore a second objective was to explore whether this potential limitation undermined the usefulness of fuel−water equilibria predictions, in comparison to other commonly used approaches for modeling the environmental fate of organic pollutants in fuels. If successful, this method would allow engineers and regulators to estimate the fuel−water partition coefficients of novel fuel constituents based on existing pure phase LSERs. As a result, LSST-derived LSERs may enable more effective screening of the environmental transport behavior of proposed fuel additives, including the potential to threaten water (*4, 6*) and urban air (*64*). Additionally, the LSST approach is not restricted to aqueous−organic systems; for example, adding $\log P_{i,l}^{\circ}$ (the hypothetical pure liquid vapor pressure of solute *i*) to both sides of eq 3 gives an LSST expression for the vapor−liquid partitioning of solute *i*. Finally, this investigation illuminates a general method whereby the predictive power of previously resolved LSERs for solvent systems might be extended to multicomponent mixtures of environmental relevance.

Methods

Literature compositions were collected for several fuels and fuel-like mixtures (Tables 1 and 2) and related ternary two-phase organic-water systems (Table 3). Individual phase mixture compositions were converted to volume fractions, assuming $\Delta V_{mixing} = 0$. Only mixture components which contributed greater than 0.1 vol % to either phase were included in the subsequent solvation modeling. In other words, substances of less than 0.1 vol % concentration in a

TABLE 2. Estimated Compositions of Retail Gasoline Mixtures Based on Survey Averages (Reported as Mass Percent) (*30, 29*)

gasoline component	conventional		oxygenated	
	mass%	calc. vol %	mass%	calc. vol %
butane	8.3	9.4	7.5	8.5
pentane	7.5	8.3	6.7	7.4
hexane	5.8	6.3	5.2	5.6
heptane	2.2	2.4	2.0	2.1
octane	2.0	2.1	1.8	1.9
2-methylpentane	5.8	6.3	5.2	5.6
2,3-dimethylbutane	4.0	4.3	3.6	3.9
2,2,4-trimethylpentane	10.6	11.2	9.5	10.1
methylcyclopentane	2.1	2.1	1.9	1.9
2-methyl-2-butene	1.8	1.9	1.6	1.7
1-hexene	3.4	3.6	3.1	3.3
benzene	4.3	3.9	3.9	3.5
toluene	16.2	14.7	14.6	13.3
xylenes	6.2	5.7	5.6	5.2
ethylbenzene	7.3	6.7	6.6	6.1
1,2,3-trimethylbenzene	9.2	8.5	8.3	7.7
naphthalene	3.3	2.8	3.0	2.5
methyl *tert*-butyl ether	0.0	0.0	10.0	9.7

given mixture were considered too dilute to influence the overall solvation properties of that phase. Where specific characterizations of fuels were not given, we assumed average gasoline or diesel compositions found in surveys (*5, 30, 32*). Uncertainties in mixture compositions of the synthetic systems were generally estimated to be less than 1 vol %, whereas variabilities of the major component concentrations in real fuel mixtures were typically between 3 and 5 vol %, depending on the component and the type of mixture (*5, 30, 32*).

To construct LSERs for fuel and fuel-like mixture systems of interest, pure solvent−water LSERs were used to describe the representative individual mixture components (Table 4). Fitted LSER coefficients for several pure solvent−water systems were directly available in the literature (*37−39, 44, 65*); for some solvents (e.g., the aliphatic alcohols), it was preferable to estimate solvent−water LSER coefficients by subtracting the corresponding solvent−air LSER coefficients from the water−air LSER coefficients (*39*). Since individual solvent−water or solvent−air LSER coefficients were not available for all of the fuel mixture components considered here, many components were grouped into "pseudocomponent" (*34*) categories as follows. Normal and branched alkanes were grouped and treated using the alkane solvent LSER; additionally, olefins were considered treatable using the alkane−water LSER as long as olefin was not a dominant fuel component (less than ∼10 vol %). Methylcyclopentane was treated using the cyclohexane LSER; and alkyl-substituted aromatic hydrocarbons and naphthalene were grouped together and modeled using the toluene LSER. Since a LSER

TABLE 3. Ternary Mixture Composition Ranges (Reported as Mass Percent in Each Phase) (67)

	water (A) benzene (B) isobutanol (C)		water (A) toluene (B) isobutanol (C)		water (A) benzene (B) pentanol (C)		water (A) benzene (B) hexanol (C)		water (A) benzene (B) MTBE (C)	
	aqueous	organic	aqueous	organic	aqueous	organic	aqueous	organic	aqueous	organic
A	91.8−99.8	0.2−19.0	91.5−99.9	0.1−17.6	97.9−99.8	0.1−11.0	99.5−99.8	0.1−7.3	95.8−100	0.1−1.4
B	0.0−0.2	0.0−99.9	0.0−0.1	0.0−99.9	0.0−0.2	0.0−99.9	0.0−0.2	0.0−99.9	0.0−0.2	3.9−99.9
C	0.0−8.2	0.0−81.0	0.0−8.5	0.0−82.4	0.0−2.1	0.0−89.0	0.0−0.5	0.0−92.7	0.0−4.2	0.0−94.7

TABLE 4. Solvent−Water and Water−Air LSER Coefficients Estimated from Published LSERs

solvent system	c	r	s	a	b	v	ref
water−air	−0.99	0.58	2.55	3.81	4.84	−0.90	(39)
alkane−water	0.29	0.65	−1.66	−3.52	−4.82	4.28	(38)
cyclohexane−water	0.13	0.82	−1.73	−3.78	−4.91	4.65	(38)
toluene−water	0.02	0.59	−0.78	−2.92	−4.57	4.53	(44)
benzene−water	0.02	0.49	−0.60	−3.01	−4.63	4.59	(44)
diethyl ether−water	0.46	0.57	−1.04	−0.02	−5.51	4.35	(44)
hexanol−water	0.04	0.47	−1.15	0.08	−4.06	4.25	(65)
pentanol−water	0.08	0.52	−1.29	0.21	−3.91	4.21	(65)
isobutanol−water	0.23	0.51	−0.69	0.02	−2.26	2.78	(37)
ethanol−water	0.21	0.41	−0.96	0.19	−3.65	3.93	(65)

was not available to describe MTBE−water systems, the diethyl ether−water LSER was used as a substitute. Using these assumptions, enough applicable solvent−water LSERs were drawn from the literature or estimated to represent all the major components for several relevant fuel formulations and their contacting aqueous mixtures. Uncertainties in LSER system coefficients (Table 4) were typically around 0.03 to 0.05.

Mixture volume fraction data were combined with estimated pure component solvent−water LSER coefficients to formulate liquid−liquid mixture LSER coefficients using eq 6. The liquid−liquid mixture LSER coefficients were then linearly combined with the solvatochromic parameters of 37 polar and nonpolar solutes (Table 5) to calculate 123 synthetic and retail fuel−water partition coefficients (listed in the Supporting Information) and 156 ternary system partition coefficients from the two-phase systems described in Table 3. Uncertainties of the LSER solute parameter values (Table 5) ranged from 0.02 to 0.04.

There were two exceptions to this straightforward protocol. For Heerman and Powers's synthetic fuel−water/ethanol system (66), the aqueous phase was set to their reported ethanol/water composition. But since the system composition depended on the calculated $K_{ethanol,fw}$ values, ethanol concentrations in the synthetic fuel phase were iteratively varied until $\phi^f_{ethanol}$ values and $K_{ethanol,fw}$ values were self-consistent using eq 6. This generated an estimated ethanol partition coefficient which could be evaluated against measured values. In the case of the fuel/MTBE−water mixture data of Schmidt et al. (5), MTBE mixture concentrations were reported in terms of initial fuel levels rather than measured postequilibration solution concentrations in either phase. For this set, an overall system mass balance of MTBE was therefore constrained, while, simultaneously, MTBE concentrations in both phases were determined via iterative calculation of ϕ^f_{MTBE}, ϕ^w_{MTBE}, and $K_{MTBE,fw}$ until eq 6 achieved self-consistency.

Results and Discussion

Three categories of fuel−water systems were separately considered. First, we report results for which the fuel phase has multiple components, but the aqueous phase is relatively pure. Second, we consider systems in which the fuel phase is a nonpolar mixture and the aqueous phase includes

TABLE 5. LSER Solute Parameters and Hypothetical Pure Liquid Vapor Pressures (38, 39, 74, 17)

solute	R_2	π_2^H	α_2^H	β_2^H	V_x	$\log P_i^o$ [bar]
water	0.000	0.45	0.82	0.35	0.167	−1.50
aniline	0.955	0.96	0.26	0.41	0.816	−3.08
p-toluidine	0.923	0.95	0.23	0.45	0.957	−1.76
o-toluidine	0.966	0.92	0.23	0.45	0.957	−3.45
2,6-dimethylaniline	0.972	0.89	0.20	0.46	1.098	−3.70
phenol	0.805	0.89	0.60	0.30	0.775	−3.14
p-cresol	0.820	0.87	0.57	0.31	0.916	−3.59
o-cresol	0.840	0.86	0.52	0.30	0.916	−3.20
3,4-dimethylphenol	0.830	0.86	0.56	0.39	1.057	−4.06
2,6-dimethylphenol	0.860	0.79	0.39	0.39	1.057	−3.26
3,4,5-trimethylphenol	0.830	0.88	0.55	0.44	1.198	−4.02[a]
2,4,6-trimethylphenol	0.860	0.79	0.37	0.44	1.198	−4.02[a]
methanol	0.278	0.44	0.43	0.47	0.308	−0.76
ethanol	0.246	0.42	0.37	0.48	0.449	−1.09
2-propanol	0.212	0.36	0.33	0.56	0.590	−1.21
tert-butanol	0.180	0.30	0.31	0.60	0.731	−1.25
isobutanol	0.219	0.39	0.37	0.48	0.872	na[c]
n-pentanol	0.219	0.42	0.37	0.48	0.872	na[c]
n-hexanol	0.210	0.42	0.37	0.48	1.013	na[c]
methyl tert-butyl ether	0.024	0.19	0.00	0.45	0.872	−0.49
ethyl acetate	0.106	0.62	0.00	0.45	0.747	−0.90
thiophene	0.687	0.56	0.00	0.15	0.641	−0.96
benzo[b]thiophene	1.323	0.88	0.00	0.20	1.010	−2.79[b]
benzene	0.610	0.52	0.00	0.14	0.716	−0.90
toluene	0.601	0.52	0.00	0.14	0.857	−1.43
ethylbenzene	0.613	0.51	0.00	0.15	0.998	−1.91
n-propylbenzene	0.604	0.50	0.00	0.15	1.139	−2.35
m-xylene	0.623	0.52	0.00	0.16	0.998	−1.96
o-xylene	0.663	0.56	0.00	0.16	0.998	−2.05
p-xylene	0.613	0.52	0.00	0.16	0.998	−1.93
1,2,3-trimethylbenzene	0.728	0.61	0.00	0.19	1.139	−2.70
4-ethyltoluene	0.630	0.51	0.00	0.18	1.139	−2.40
naphthalene	1.340	0.92	0.00	0.20	1.085	−3.33
1-methylnaphthalene	1.344	0.90	0.00	0.20	1.226	−4.08
2-methylnaphthalene	1.304	0.88	0.00	0.20	1.226	−3.95[a]
acenaphthene	1.604	1.05	0.00	0.20	1.259	−4.67
fluorene	1.588	1.06	0.00	0.20	1.357	−4.75
phenanthrene	2.055	1.29	0.00	0.26	1.454	−5.36
anthracene	2.290	1.34	0.00	0.26	1.454	−5.35
fluoranthene	2.377	1.55	0.00	0.20	1.585	−7.15[a]

[a] Log P_i^o value estimated using ref 75. [b] Log P_i^o value taken from ref 76. [c] Not applicable.

substantial ethanol. Finally, we describe results for a few ternary systems in which polar and nonpolar solvent components are significant constituents of both the aqueous and organic phase. The compilation of measured and calculated K_{fw} values (excluding the ternary systems in Table 3) is given in the Supporting Information.

Partitioning of Polar and Nonpolar Compounds between Synthetic or Retail Fuels and Water. In both simulated and realistic fuel−water systems, LSST-derived LSERs predicted the partitioning behavior of 88 polar and nonpolar solutes within a factor of 3 of measured K_{fw} values, despite simplifications (e.g., assuming the alkene solvent fraction could be described by alkanes) and without the aid of any fitting procedures (root-mean-squared error, rmse$_{\log K}$ = 0.43; Figure 1A). Reported or estimated uncertainty in partition coefficient measurements was significantly lower, typically ranging from 0.05 to 0.12 in the log K_{fw} (5, 21, 66, 67). The model captured
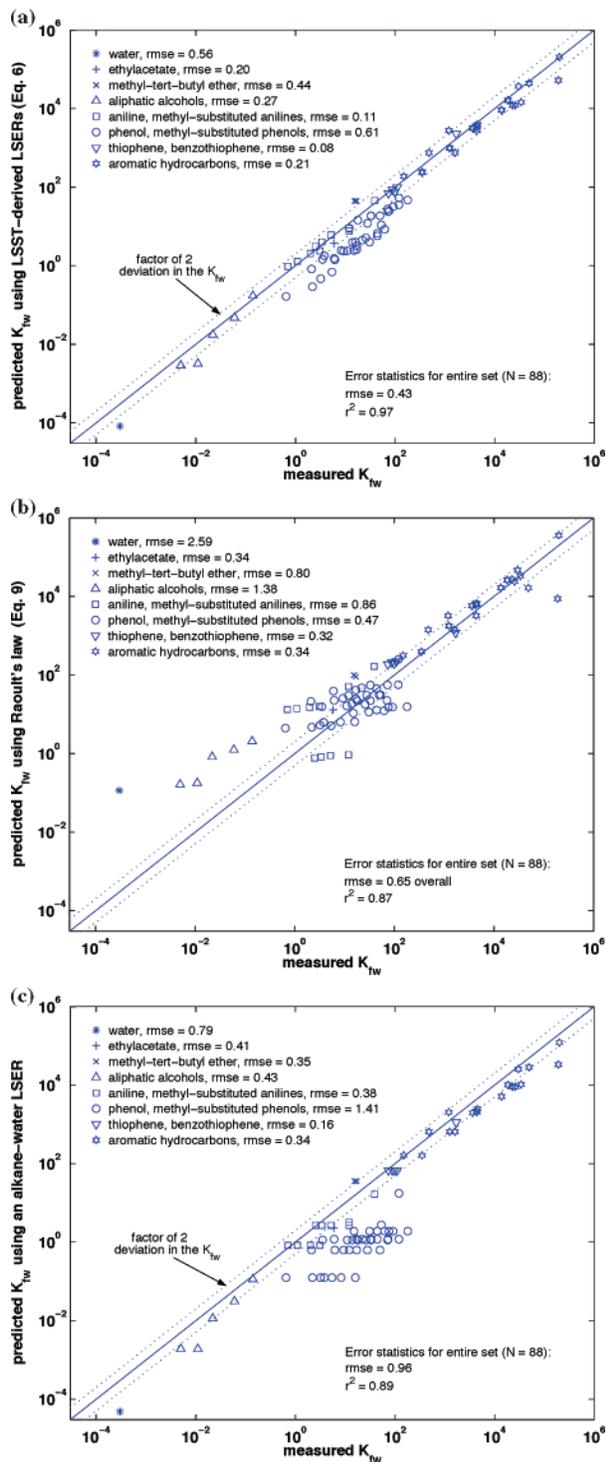
FIGURE 1. Predicted K_{fw} values of polar and nonpolar compounds in simulated and retail fuel−water systems (A) using LSST-derived LSERs (eq 6), (B) assuming Raoult's law for the fuel phase (eq 9), or (C) using the alkane−water LSER (Table 4).

nonpolar solute behavior better than average ($rmse_{\log K} = 0.21$). The partition coefficient predictions of phenols and methyl-substituted phenols were the most inaccurate ($rmse_{\log K} = 0.61$), especially in systems containing MTBE. Across all other solute families under consideration (i.e., not phenols), including nonpolar aromatic hydrocarbons, anilines, aliphatic alcohols, methyl *tert*-butyl ether, ethyl acetate, thiophenes, and water, the LSST-derived LSERs gave results that were almost as good as the nonpolar solute set alone ($rmse_{\log K} = 0.23$).

Failure of the LSST approximation for polar solutes in the organic phase could largely explain LSST-derived LSER deviations. In this set of systems, major fuel components are sufficiently hydrophobic that the solvation properties of the aqueous phase were likely to be unaffected by the presence of fuel phase constituents. The most abundant aqueous phase organic component was MTBE in system 6 (Table 1), having aqueous phase concentrations as high as 0.067 M ($\phi_{MTBE}^{w} = 0.008$) in this case. Since LSERs can model pure water−air partitioning accurately ($\sigma_{\log K} = 0.15$ (*39*)), we inferred that model error for these systems was primarily related to treatment of the organic phase. Additionally, consistent trends were detectable in model residuals. The error for phenol log K_{fw} predictions was $rmse_{\log K} = 0.45$ in 5% MTBE mixtures, $rmse_{\log K} = 0.63$ in 15% MTBE mixtures, and $rmse_{\log K} = 0.68$ in 30% MTBE mixtures ($N = 10$ in all three cases); thus the bias of phenol K_{fw} predictions systematically increased with increasing MTBE content in the organic phase, if other considerations were held equal. Additionally, across predictions for all solutes, a significant correlation ($r^2 = 0.60$) was found between negative model residuals and solute α_2^{H} (hydrogen-bond donating parameter) values. In other words, the LSST-derived LSER model increasingly underpredicted K_{fw} values as solute hydrogen bond donating capability increased, across all solutes. Since LSST becomes less accurate in cases where solute polarity exceeds that of the solvent, we surmised that strong hydrogen-bond solute−solvent interactions (e.g., phenol−MTBE complexes) in the organic phase were primarily responsible for LSST-derived LSER deviations. It was confirmed that measured phenol and aniline K_{fw} values are independent of concentration at their observed abundances in fuel (*68*), indicating that they probably behave as dilute solutes.

We pursued separate modeling of the organic phase as an ideal solution (Raoult's law). A comparison of the accuracy of Raoult's law predictions versus LSST-derived LSER predictions demonstrates whether the latter model can meaningfully capture nonideal solvation of both nonpolar and polar solutes in the organic mixture phase. Raoult's law is frequently used to model nonpolar solutes in fuels and related mixtures (*21−27*). In this case, the fuel−water partition coefficient may be expressed as (*17, 69*)

$$K_{i,fw} = K_{i,fa}K_{i,aw} = \frac{RT}{V_f P_{l,i}^{\circ}}K_{i,aw} \qquad (8)$$

where $K_{i,fa}$ is the fuel−air partition coefficient of solute i, $K_{i,aw}$ is the air−water partition coefficient of solute i, R is the molar gas constant, T is temperature, V_f is the molar volume of the fuel phase, and $P_{l,i}^{\circ}$ is the (hypothetical) liquid vapor pressure of solute i. Raoult's law would be inappropriate for modeling the aqueous phase, since nonpolar organic solutes are known to experience significant nonideality in aqueous conditions (*70*). If we apply Raoult's law to the fuel phase, but continue to use an air−water LSER (*39*) to treat the aqueous phase, we find

$$\log K_{i,fw} = \log \left[\frac{RT}{V_f P_l^{\circ}} \right] - (c_{aw} + r_{aw}R_2 + s_{aw}\pi_2^{H} +$$
$$a_{aw}\alpha_2^{H} + b_{aw}\beta_2^{H} + v_{aw}V_x) \quad (9)$$

Eq 9 accurately predicted fuel−water partitioning of a wide range of nonpolar hydrocarbon and thiophene compounds (Figure 1B), in agreement with previous findings (*21, 23, 25, 27*). However, predictions were highly unreliable for polar solutes, since nonideal solvation typically occurs in cases where the solute and solution differ significantly in polarity and/or hydrogen-bonding capabilities (*69*). These results were consistent with our expectation that Raoult's law is an inadequate model for describing the behavior of polar solutes in fuels.
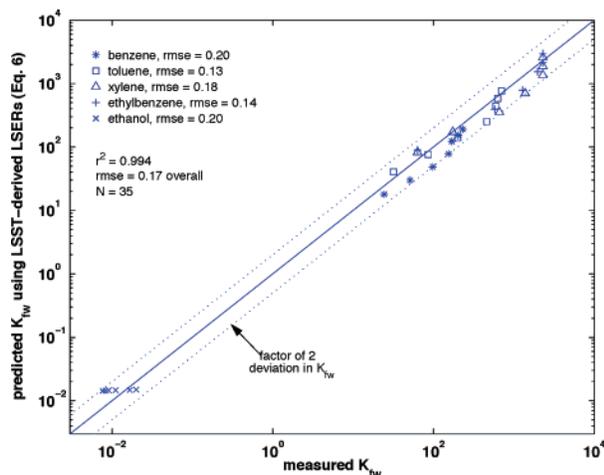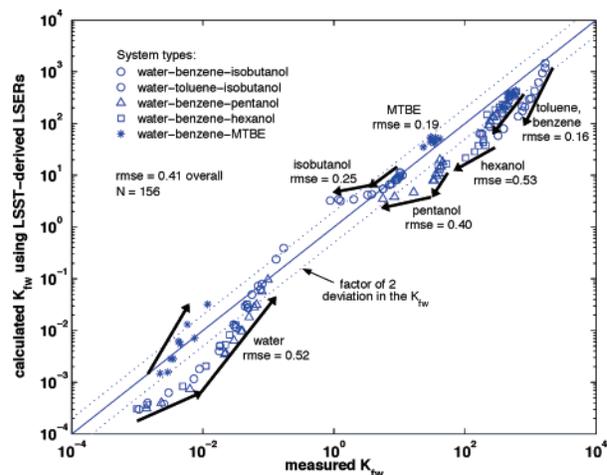
FIGURE 2. Predicted K_{fw} values of BTEX and ethanol in synthetic fuel systems with ethanol amendments using LSST-derived LSERs (eq 6).

FIGURE 3. Calculated K_{fw} values for two-phase ternary benzene/toluene−aliphatic alcohol−water and benzene−MTBE−water mixtures using LSST-derived LSERs. Symbols indicate type of system; text labels indicate the system component that was treated as the solute. For example, the K_{fw} values of water solute in the water−benzene−pentanol mixture systems are shown as "△" near the "water" label. The "→" symbols indicate the K_{fw} trend with addition of oxygenate (MTBE or alcohol).

Additional calculations were conducted to test whether the LSST-derived LSER model could effectively distinguish between solvation in real fuel mixtures and solvation controlled only by London dispersion interactions with alkanes. Across 7 out of 8 solute families, fuel−water partitioning calculations using the alkane−water LSER (Table 4, (38)) gave significantly poorer predictions (Figure 1C) than the LSST-derived LSER approach. Using the alkane−water LSER, solvation of polar solutes in the organic phase, particularly for phenols and anilines, was underpredicted by 1−2 orders of magnitude in the partition coefficient, K_{fw}. Additionally, alkane−water LSER predictions of nonpolar solute partitioning between gasolines or diesel fuel and water was significantly biased low compared to LSST-derived LSER predictions. The alkane−water LSER biases found for both polar solutes and non-hydrogen bonding solutes demonstrated that, to an important extent, LSST-derived LSERs captured the increased solvency of the fuel phase resulting from the presence of both aromatic hydrocarbon compounds and MTBE.

Partitioning of Aromatic Hydrocarbons and Ethanol in Synthetic Fuel−Water/Ethanol Mixtures. Synthetic fuel−water systems containing 5 to 50 vol % ethanol in the aqueous phase (66) reflect a more typical application of LSST, in which LSST is used to extrapolate the solubility of solutes in water modified with a miscible organic cosolvent (53). The partitioning behavior of both nonpolar aromatic solutes and a polar solute, ethanol, were predicted using LSST-derived LSERs (rmse$_{log K}$ = 0.17; Figure 2). These results confirm previous applications of LSST to solute partitioning in fuel−water/cosolvent systems (27, 54, 55). In addition, fuel−water/ethanol mixture calculations showed that LSST-derived LSERs could treat mixtures in both the aqueous and organic phase, consistent with results discussed in the previous section.

Partitioning of Benzene/Toluene−Alcohol−Water Systems and Benzene−MTBE−Water Mixtures. In ternary systems containing either benzene or toluene, water, and a C_4 to C_6 aliphatic alcohol (Table 3; Figure 3), partitioning of all three components (including water) was calculated to within factors of 2 to 4 of observed K_{fw} values (rmse$_{log K}$ = 0.41). The LSST-derived LSER model correctly predicted that aliphatic alcohols partition primarily into the organic phase in all of the systems studied (i.e., K_{fw} > 1 for these solutes). The model also correctly captured the trend that addition of aliphatic alcohol cosolvent moved the K_{fw} of all solutes closer to unity (as indicated by the thick arrows in Figure 3), indicating that polar compounds in the fuel mixture and nonpolar compounds in the aqueous mixture were both

accommodated by increased cosolvent concentrations. However the calculated K_{fw} values for water and the aromatic hydrocarbons were generally biased low: as the abundance of aliphatic alcohol was increased, solvation in the organic phase was more favorable for the water and aromatic hydrocarbon solutes than was indicated by the LSST-derived LSER model. By comparison, in benzene−MBTE−water systems, the model accurately calculated the partitioning of all three components over the entire range of compositions considered (rmse$_{log K}$ = 0.18). In agreement with previously discussed results, LSST-derived LSERs could make meaningful partitioning predictions (rmse$_{log K}$ ∼ 0.4) of both polar and nonpolar solutes, given prior knowledge of the ternary system compositions.

However, if mixture composition information was not provided to set the volume fractions needed in the LSST-derived LSERs for the ternary systems, computed results were considerably worse. Iterative calculation of eq 6 for ϕ and K_{fw} values to self-consistency under mass conservation constraints produced only order-of-magnitude accuracy for K_{fw} predictions of ternary mixture components (rmse$_{log K}$ = 0.98, data not shown). LSST-derived LSERs made inadequate predictions using mass conservation calculations for these ternary systems because the organic phase was typically composed of a high water content (5 to 20 vol %). Moderate errors in the calculated water content of the organic phase propagated to considerable changes in the mixture LSER coefficients. This in turn led to exponentially magnified errors in predictions of both water partitioning and that of other components. We therefore expect LSST-derived LSERs to make inaccurate composition predictions for systems in which highly polar compounds (e.g., water) significantly constitute the organic phase.

Comparison of LSST-Derived LSERs to the Solvent Compartment Mixing Model. To make comparisons with an alternative solvation model for fuel−water systems, we developed a contrasting approach to model the fuel phase, based on the "solvent compartments" mixing rule suggested by Schmidt et al. (5, 71). Schmidt and co-workers proposed that the partition coefficient of a solute i partitioning between a fuel mixture p and relatively pure water phase w could be modeled as

$$K_{i,pw} = \sum_j \phi_j^p K_{i,jw} \qquad (10)$$

where multiple components j constitute the fuel phase. This approach is mathematically equivalent to a hypothetical system in which the solute partitions between pure water and a composite of pure solvent compartments that constitute the total fuel mixture p, where ϕ_j^p represents the volume of each fuel component j compartment as a fraction of the total fuel volume. This approach was very useful for the set of systems that Schmidt et al. considered; however, it is not clear how eq 10 should extend to systems in which the aqueous phase also contains abundant cosolvent(s). We adapted this approach by using the solvent compartment model to treat the fuel phase and applying LSST to the aqueous phase, as follows. The partitioning of solute i between a mixed fuel phase p and mixed aqueous phase q may be described as

$$\log K_{i,pq} = \log \left(\frac{K_{i,pw}}{K_{i,qw}} \right) \qquad (11)$$

where the fuel−water partition coefficient, $K_{i,pw}$, can be treated using eq 10 and the hypothetical aqueous mixture−water partition coefficient, $K_{i,qw}$, may be modeled using LSST (eq 6), so that

$$\log K_{i,pq} = \log \left(\sum_j \phi_j^p K_{i,jw} \right) - \sum_k \phi_k^q \log K_{i,kw} \qquad (12)$$

Substituting eq 2 into eq 12, we find

$$\log K_{i,pq} = \log \left(\sum_j \phi_j^p 10^{(c_{jw}+r_{jw}R_2+s_{jw}\pi_2^{\mathrm{H}}+a_{jw}\alpha_2^{\mathrm{H}}+b_{jw}\beta_2^{\mathrm{H}}+v_{jw}V_x)} \right) - \sum_k \phi_k^q \left(c_{kw} + r_{kw}R_2 + s_{kw}\pi_2^{\mathrm{H}} + a_{kw}\alpha_2^{\mathrm{H}} + b_{kw}\beta_2^{\mathrm{H}} + v_{kw}V_x \right) \qquad (13)$$

We refer to eq 13 as the "combined solvent compartment/LSST" (CSCLSST) mixing rule for LSERs. Following the protocol previously described for LSST-derived LSERs in the Method section, we grouped solvent components for each phase and applied the resulting pseudocomponent volume fraction estimates and pure solvent−water LSER coefficients (Table 4) to eq 13, thereby giving CSCLSST-LSER calculated K_{fw} estimates.

The CSCLSST-LSER model predicted fuel−water partitioning with accuracy comparable to LSST-derived LSERs for the 279 K_{fw} data considered here (rmse$_{\log K}$ = 0.4 overall for both methods), but the two models exhibited different biases. CSCLSST-LSER K_{fw} predictions for the realistic and synthetic fuel−water systems in Tables 1 and 2, including mixtures with ethanol amendment, were usually within a factor of 2 of measured values (rmse$_{\log K}$ = 0.26, N = 123, Figure 4). The worst deviations were for substituted phenol solutes in isooctane/MTBE−water systems (rmse$_{\log K}$ = 0.48); these K_{fw} values were systematically overpredicted by the CSCLSST-LSER approach. The model performed considerably worse for the ternary mixtures in Table 3 (rmse$_{\log K}$ = 0.47, N = 156; data not shown), severely overpredicting the partition coefficients of water in particular (rmse$_{\log K,\text{water}}$ = 0.76). By comparison, LSST-derived LSERs typically under-predicted the K_{fw} values of substituted phenols (in real and simulated fuel−water systems) and water (in ternary systems). A broader discussion of CSCLSST-LSER results is presented elsewhere (72).

Synthesis of Results. Applicability of the LSST-derived LSER approach rests on the conditions that (a) LSERs are an adequate model for characterizing solute partitioning in mixture systems; (b) LSST is a reliable mixing rule; and (c)
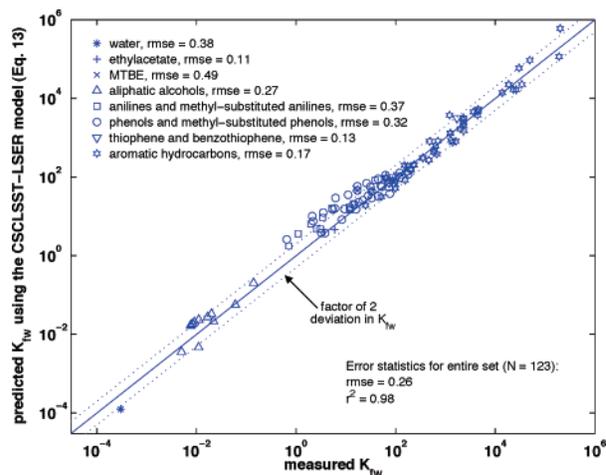
FIGURE 4. Predicted K_{fw} values of polar and nonpolar compounds in simulated and retail-water systems, including systems containing ethanol amendments, using the CSCLSST-LSER model (eq 13).

the mixture solvation properties can be accurately extrapolated from dilute solute conditions. Of these three assumptions, the first was considered unlikely to contribute dominantly to model failure, since the accuracy of LSER-predicted solvation energies is about rmse$_{\log K,\text{ LSER}}$ = 0.16 for a wide range of solvents and mixtures. Model error related specifically to the LSST mixing rule assumption could be estimated using first-order error propagation analysis (73), assuming that uncertainties associated with the LSER model, K_{fw} measurements, and the LSST mixing rule were uncorrelated. K_{fw} measurement errors were considered rmse$_{\log K,\text{ meas}} \sim 0.08$ for the studies considered here. We estimated that uncertainty in fuel compositions may contribute an error of up to 0.05 in the calculated log K_{fw} values of solutes in the real fuel−water systems. Given rmse$_{\log K}$ = 0.4 overall for LSST-derived LSERs and accounting for these sources of uncertainty, the LSST mixing rule error was thus estimated to be rmse$_{\log K,\text{ LSST}}$ = 0.3 (including inaccuracy due to extrapolation from infinite dilution conditions). This is comparable to the previous results of Li (63), in which the LSST approximation was shown to have an average absolute error ranging from 0.1 to 0.4 log K units for binary mixtures (depending on the type of cosolvent). For the systems studied by Li, LSST tended to perform best when the mixture was dominated by one solvent ($\phi \sim 0.80$ or more) and when the solute was less polar than the mixture (63). A similar analysis of the CSCLSST-LSER results suggested a CSCLSST mixing rule error of 0.3 in the log K_{fw}.

The results shown here suggest that both the LSST-derived LSER and CSCLSST-LSER models captured the effect of most polar cosolvent amendments (e.g., aromatic hydrocarbons or MTBE that are capable of electron donation) to a nonpolar solvent (alkanes). However, the likelihood of hydrogen-bonding solutes to be solvated by complementary solvent components in the nonpolar phase may be underpredicted by LSST. LSST-derived LSER predictions were generally biased low for hydrogen-bond donors such as phenol in synthetic fuel−water systems. Likewise, the calculated partition coefficient of water between an aqueous and mixed water−alcohol−hydrocarbon phase was biased low by as much as 1.0 log K unit. Systematic predictive bias of this magnitude was not generally observed for other polar and nonpolar solute families having substantially lower hydrogen-bond acidities. In contrast to LSST-derived LSERs, the CSCLSST-LSER model usually overpredicted the fuel−water partitioning of strongly hydrogen-bond donating solutes (e.g., phenols and water), particularly if hydrogen-bond accepting solvents (e.g., MTBE or water) were abundant in the organic phase.

Hence, whereas LSST appears to underestimate the importance of hydrogen-bonding interactions in the organic phase, we concluded that the compartment solvent model overestimates these interactions in the organic phase. Since the two models appear to exhibit opposite biases for polar solutes, they could be used to generate bounding K_{fw} estimates.

A fuel−water mixtures partitioning model which can be applied to a wide range of environmental solutes is needed. Although Raoult's law is commonly applied for estimating solute partitioning into environmental mixtures, it is inadequate for polar solutes in relatively nonpolar mixtures. The LSST-derived LSER and CSCLSST-LSER approaches do not calculate solute partitioning behavior in mixtures as accurately as LSERs derived from original data. Additionally, the fuel−water mixtures considered here do not reflect a broad evaluation of either model for organic and aqueous mixtures. For example, these simple mixing rules are likely to fail for systems containing surfactants or other compounds which create such highly ordered solvation structures. However, this work suggests that the LSST-derived LSER and CSCLSST-LSER models are suited for common fuel mixtures. The results may also inspire evaluation of these methods for other environmentally relevant media. Once the mixture LSER coefficients for an organic-water mixture system have been estimated, solvation energies for a broad set of solutes may be calculated. This is not true of other conventional approaches such as UNIFAC (*13*−*15*), which frequently lack the interaction parameters necessary to estimate the behaviors of solutes in fuel mixtures (*29*).

Previous research suggests that LSERs can accurately model partitioning in a range of organic mixtures (*35*, *36*, *62*). The challenge, then, lies in finding a general method to estimate the best LSER coefficients for such mixtures, in the absence of the copious data required for a conventional regression analysis. In this study, we used the linear solvent strength approximation to generalize the application of pure-phase LSER coefficients to a range of mixtures. The resulting model predictive error for solutes in synthetic and realistic fuel systems composed of nonpolar hydrocarbons and MTBE or alcohols was estimated to be ∼0.4 in the log K. This level of accuracy is suitable for many applications in environmental fate analysis of organic pollutants.

Acknowledgments

Supporting Information Available

Table of LSST-derived LSER and CSCLSST-LSER model predictions vs experimental partition coefficient values of polar and nonpolar compounds in various fuel−water systems. This material is available free of charge via the Internet at http://pubs.acs.org.

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