Partitioning of Aromatic Constituents into Water from Gasoline and Other Complex Solvent Mixtures

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■ Variations in gasoline composition (source variations) as well as complexity in composition (nonideal behavior, cosolvent effects) contributing to variability in gasoline–water partitioning of aromatic hydrocarbon constituents were examined. Aromatic hydrocarbon concentrations in water extracts of 31 gasoline samples varied over 1 order of magnitude, reflecting the diversity in gasoline composition. However, the gasoline–water partition coefficients (K_{fw}) varied by less than 30% among these samples. Partitioning between water and known mixtures of aromatic and aliphatic solvents was measured and used to estimate the upper and lower bounds of K_{fw} values for more complex solvent mixtures such as gasoline and diesel fuel. Oxygenated additives, such as methanol and methyl *tert*-butyl ether (MTBE), were shown to have minimal cosolvent effects on hydrocarbon partitioning. The observed inverse, log–log linear dependence of K_{fw} values on aqueous solubility could be well predicted by assuming gasoline to be an ideal solvent mixture (i.e., Raoult's law is valid).

Introduction

The release of organic compounds from nonaqueous-phase liquids (NAPL) in subsurface environments can be estimated from the distribution coefficient (K_d) for that solute between the water and organic phases; for a fuel organic phase, this parameter is designated here by K_{fw}. Fluid-phase equilibria have been extensively studied and numerous texts, reviews, and data compilations have been published (1–3). Under equilibrium conditions, the thermodynamic activity of each component is the same in both phases:

$$X_i^w a_i^w = X_i^o a_i^o \qquad (1)$$

where the subscript *i* denotes component *i*, *X* is mole fraction concentration, *a* is activity coefficient; and the superscripts w and o denote water and organic phases, respectively. The distribution coefficient based on mole fraction (K_x) is defined as the ratio of the infinite dilution activity coefficients (a^∞):

$$K_x = X_i^o / X_i^w = a_i^{\infty,w} / a_i^{\infty,o} \qquad (2)$$

For liquid–liquid partitioning, a distribution coefficient, K_d, can also be defined as a ratio of solute concentrations in the organic and water phases, i.e.

$$K_{d,i} = C_i^o / C_i^w \qquad (3)$$

where C^o and C^w are solute concentrations (mol/L) in the organic and aqueous phases, respectively and the subscript *i* designates the *i*th solute. Mixtures of structurally related hydrophobic liquids have activity coefficients equal to 1 in the organic phase ($a_i^o = 1$). Under these conditions, solute concentration in the aqueous phase (C_i^w) follows Raoult's law (4) and is proportional to the mole fraction

Table I. Composition of Leaded and Unleaded Gasolines[a,b]

compound	unleaded	leaded
normal/iso hydrocarbons	55	59
isopentane	9–11	9–11
n-butane	4–5	4–5
n-pentane	2.6–2.7	2.6–2.7
aromatic hydrocarbons	34	26
xylenes	6–7	6–7
toluene	6–7	6–7
ethylbenzene	5	5
benzene	2–5	2–5
naphthalene	0.2–0.5	0.2–0.5
benzo[*b*]fluoranthene	3.9 mg/L	3.9 mg/L
anthracene	1.8 mg/L	1.8 mg/L
olefins	5	10
cyclic hydrocarbons	5	5
additives		
tetraethyllead		600 mg/L
tetramethyllead		5 mg/L
dichloroethane		210 mg/L
dibromoethane		190 mg/L

[a] Adapted from Watts (14). [b] Unless otherwise noted, values are in volume percent.

of solute in the organic phase. Thus, $C_i^w = X_i^o S_i^w$, where S_i^w is the aqueous solubility (mol/L) of neat solute. Assuming the organic phase to be an ideal mixture of liquids, eq 3 can be restated as

$$K_{d,i} = \frac{C_i^o}{X_i^o S_i^w} = \frac{10^3 (\delta / \overline{MW^o})}{S_i^w} \qquad (4)$$

where δ is the organic liquid density (g/mL) and $\overline{MW^o}$ is the *average* molecular weight for the organic phase. It is evident from eq 4 that an inverse relationship between $K_{d,i}$ and S_i^w is expected; the plot will have a unit slope and the intercept is dependent on the density and the average molecular weight of the organic phase.

Solute concentrations in water resulting from contact with an immiscible mixture containing components that interact in the solvent phase show deviations from ideal behavior. The activity coefficients to explain these deviations can be estimated by the UNIFAC model (1). Specific deviations from ideal behavior were reported from mixtures of aromatic hydrocarbons and saturated paraffins (5, 6). These deviations resulted in higher aqueous concentrations (10–20%) than predicted from the ideal behavior.

Gasoline is a complex mixture of volatile hydrocarbons. The major components are branched-chain paraffins, cycloparaffins, and aromatic compounds. The specific composition will vary depending on the source of the petroleum as well as the production method (e.g., distillation or fractionation, thermal and catalytic cracking, re-forming, isomerization). Gasoline may also include a number of additives (dyes, antiknock agents, lead scavengers, antioxidants, metal deactivators, corrosion inhibitors, volatilty/octane enhancers) (7, 8).

The approximate volume percent composition of unleaded and leaded gasoline is given in Table I. Unleaded gasoline generally has a higher fraction of aromatic hy-

drocarbons than leaded brands. These "lead-free" brands contain no more than 0.05 g of lead/gal. The use of tetraethyllead as an antiknock agent has been phased out for environmental and health reasons. The use of high-octane oxygenated blending agents in gasoline, e.g., methyl *tert*-butyl ether (MTBE), has increased since the phase-down of lead in gasoline began in 1975. The concentrations of these oxygenated additives may vary among states, although EPA waivers currently allow up to 15% by volume (ca. 2.7% oxygen) of MTBE in unleaded gasoline, while the oxygen content in alcohols or alcohol mixtures is allowed to be as high as 3.5 wt %.

The addition of polar organic solvents that are completely miscible or highly soluble in water (e.g., methanol, ethanol, *tert*-butyl alcohol, MTBE) to a mixture of hydrocarbons and water has a potential cosolvent effect, resulting in an increased aqueous concentration of hydrocarbons (9–11). One of the methods for estimating the solubility of a solute in a water–cosolvent mixture is based on a log–linear model. The expected solubility of a component in a water–cosolvent mixture can be estimated as (10)

$$\log S^m = \log S^w + \sigma f_c \tag{5}$$

where $\sigma = \log(S^c/S^w)$ and is an index of the solubilizing power of the cosolvent; S is the component solubility (mg/L), with the superscripts w, c, and m designating water, neat cosolvent, and mixed solvent, respectively; and f_c is the volume fraction of the cosolvent. Groves (9) reported that there was no cosolvent effect for MTBE concentrations up to mole fractions of nearly 0.2 in the hydrocarbon phase, while methanol and ethanol had an effect at sufficiently high concentrations of alcohol.

Prausnitz et al. (1) stated that liquid–liquid equilibria were much more sensitive than vapor–liquid equilibria to small changes in the effect of composition on activity coefficients. Therefore, calculations for liquid–liquid equilibria should be based, whenever possible, at least in part, on experimental liquid–liquid equilibrium data. Calculations become increasingly difficult for larger numbers of components.

The difficulties in applying the above partitioning calculations to commercial gasoline mixtures include the large number of components involved and the problem of determining the moles of each in theoretically infinite combinations. One approach has been the estimation of fuel–water partition coefficients (K_{fw}), which are based on weight percent or concentration in the fuel rather than mole fraction.

Brookman et al. (12) reported a model for estimating the concentration of a component present in the aqueous phase based on the solubility and weight percentage in the gasoline. This approach was further examined in a laboratory study (12) on the solubility of petroleum hydrocarbons in groundwater, where a reference, regular, unleaded gasoline (API PS-6) was equilibrated with organic-free, deionized water.

The partitioning of components into water is affected by the solubility of each compound in pure water and the gasoline composition. The partitioning of fuel components can be described by a partition coefficient based on the following equation (12):

$$K_{fw} = C_f/C_w \tag{6}$$

where K_{fw} is the fuel–water partition coefficient, C_f is the concentration of component in fuel (mg/L), and C_w is the concentration of component in water (mg/L).

There are greater sources of variation in values of fuel–water partition coefficients to describe gasoline com-

ponent partitioning than found for measurements of octanol–water partition coefficients (K_{ow}). K_{ow} is measured by using low solute concentrations and is a weak function of solute concentration (13). For gasoline, the concentrations of particular gasoline components may be as high as 20% of the fuel layer. Furthermore, the composition is variable, resulting in variable mole fractions for a single component concentration. Finally, certain gasoline components may be cosolvents or change the activity coefficients in the solvent phase.

Gasoline composition will vary in different parts of the country and at different times of the year. Product composition may change daily depending on refinery operations and continues to change in response to changes in regulations, for example, the phase-out of lead. In addition, independent service stations may obtain product from different suppliers depending on market conditions. All of these factors contribute to variability in gasoline composition and changes will continue to occur in the future.

Prediction of groundwater contamination with hydrocarbons when gasoline leaking from storage tanks reaches the water table is one of the major environmental concerns. The foregoing discussion suggests that estimation of hydrocarbon concentrations in groundwater that is in contact with gasoline is confounded by variation in composition depending on the source and the potential for nonideal behavior because of complex composition. These issues provided the motivation for the present study. Our primary objectives were to (1) evaluate concentration ranges of major components in water extracts of various gasolines, (2) measure fuel–water partition coefficients for major hydrocarbon components by using gasoline and mixtures of aliphatic and aromatic solvents, and (3) assess the behavior of oxygenated additives and their effect on partitioning of hydrocarbons.

Materials and Methods

Liquid–liquid partition coefficients were determined by measurements of the solute concentrations in the organic and aqueous phases by gas chromatography with flame ionization detection (GC/FID). A separate set of experiments was also conducted with ^{14}C-labeled solutes.

One objective of the gasoline partitioning study was to examine the variability in gasolines and how this affects the measured K_{fw}. Gasoline samples used in our study were obtained from the Florida Department of Agriculture and Consumer Services (DACS). As a part of the regulatory monitoring program, DACS field inspectors routinely collect gasoline samples from underground and aboveground storage tanks throughout Florida. These fuel samples are then shipped to the DACS Petroleum Laboratory in Tallahassee, FL, and are analyzed to assess compliance with ASTM guidelines. The gasoline samples we used represented both summer and winter blend of gasolines collected over a 6-month period in north and central Florida. Subsamples were obtained from the DACS Petroleum Laboratory in 40-mL volatile organic analysis (VOA) screw cap vials with Teflon-lined septa and stored on ice prior to analysis.

Additional gasoline samples were also collected from selected gas stations in Gainesville, FL. Samples were obtained from the pump in gasoline safety containers and then a subsample was transferred to a 40-mL VOA vial and cooled.

Procedures for evaluating the partitioning of gasoline constituents into the aqueous phase have been reported (12); maximum aqueous-phase concentrations of aromatic compounds were measured after a contact time of 2 h. Samples were then centrifuged to separate the two liquid

phases. Coleman et al. (15) determined that a rotation contact time of 30 min and an equilibrium period of approximately 1 h produced consistent results and that longer periods had little effect on the final concentrations.

For the GC/FID study, saturated, equilibrated solutions of neat gasolines in contact with distilled, deionized, organic-free water were prepared. Two milliliters of gasoline was added to 40 mL of water in VOA vials having Teflon septa. Samples were mixed on a rotating disk apparatus for 30 min at 22 ± 1 °C. The vials then sat undisturbed for 1 h, in an inverted position. Each separated water phase was removed through the septum at the bottom of the VOA bottle with a 5-mL syringe. Triplicate samples of each water phase were then sealed in 2-mL crimp-seal vials and refrigerated until the GC analysis was performed, typically within 2 days.

Analyses for gasoline constituents were performed by GC/FID, using a Perkin-Elmer Model 8140 gas chromatograph with a 30-m-long wide-bore capillary column (J&W, DB-1) having a 3-μm film thickness. The neat gasoline samples were analyzed by direct injection of 0.05 μL of the fuel. Gasoline components dissolved in water were determined by sparging volatiles from water with a Tekmar LSC-2 purge-and-trap instrument interfaced to the Perkin-Elmer GC. The temperature program for both neat gasolines and water extracts included a 13-min hold time at 35 °C, temperature ramping at 3 °C/min to 90 °C, and then at 5 °C/min to 200 °C. The helium carrier gas flow rate was 3.0 mL/min.

The concentration of a particular component in the fuel was based on the area percent determined in the analysis, which was assumed to approximate the weight percent of that compound. This was converted to concentration (g/L) based on an average density for gasoline of 0.74 g/mL (12).

Some overlap or incomplete peak resolution occurred in the early eluting compounds in the neat gasoline samples and to a lesser extent in the water extracts, limiting the use of this technique for selected constituents. For example, the oxygenated additive, MTBE, has a high aqueous solubility and is easily quantified in the water extract. However, it has a lower FID response than the hydrocarbons and coeluted early in the chromatogram with other hydrocarbons, making accurate quantitation in the organic phase difficult with this technique. Partition coefficients for this compound were measured in selected gasoline samples by addition of a known volume of MTBE to a gasoline that did not previously contain this additive.

Extractions for partitioning of ^{14}C-labeled solutes were conducted in 4-mL vials. The organic solvent and water were placed in the vials, spiked with the labeled solute, sealed with a Teflon-lined cap, and rotated, typically 1-3 h. Vials were centrifuged at 200g prior to sampling. The organic phase was first sampled with a glass syringe, and the remainder was removed with a glass disposable pipet. The aqueous phase was then sampled by using a glass syringe. The reliability of this method for determining liquid-liquid partition coefficients was evaluated by also measuring octanol-water partitioning of selected components by this technique. The results agreed with K_{ow} values reported in the literature for benzene, toluene, and naphthalene.

Concentrations of the ^{14}C-labeled compounds in the aqueous and organic phases were measured by liquid scintillation techniques. A Searle Delta 300 liquid scintillation counter was used to measure ^{14}C activity.

Results and Discussion

Gasoline Composition. The variability in composition and partitioning behavior of individual gasoline compo-

NEAT GASOLINE
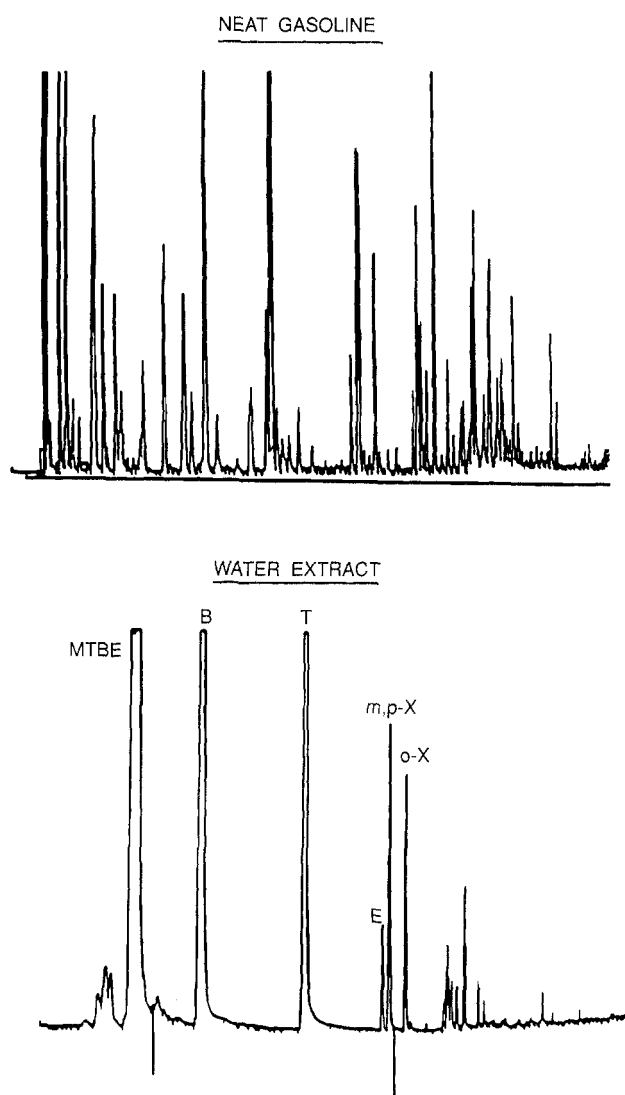
WATER EXTRACT

Figure 1. Sample chromatograms for GC/FID analysis of a neat gasoline and a water extract. Major components in the water extract identified are methyl *tert*-butyl ether (MTBE), benzene (B), toluene (T), ethylbenzene (E), *m*- and *p*-xylene (*m*,*p*-X), and *o*-xylene (*o*-X).

nents in various grades and brands of gasolines analyzed by GC/FID were evaluated for 31 gasoline samples. The hydrocarbons that partition into the aqueous phase are predominantly aromatic compounds, including benzene, toluene, and xylenes. MTBE and other oxygenated additives are highly water soluble additives, which can be identified in the aqueous phase if they are present in a given brand of gasoline.

Analyses of the water extracts produced simplified chromatograms compared to the analysis of the neat gasoline, as shown in an example in Figure 1. The chromatogram of a neat gasoline may show as many as 180 peaks, whereas a water extract typically showed 40-80 peaks under the analytical conditions employed. The water extracts usually contained ~10 peaks that had area percentages greater than 1.0.

There was considerable variability in the concentrations of constituents measured in the aqueous extracts of the gasolines. However, attempts to group gasoline brands or grades based on these differences were not generally successful. The concentration range of constituents identified in the aqueous extracts and the range in weight percent in the fuels are summarized in Table II.

Four of the gasoline samples contained MTBE, but these four did not represent either a single brand or a grade.

Table II. Variations in Gasoline Composition and Aqueous-Phase Concentration of Fuel Components in 31 Gasoline Samples

compound	gasoline compstn, wt % av (min–max)	SD	aq-phase conc, mg/L av (min–max)	SD
benzene	1.73 (0.7–3.8)	0.68	42.6 (12.3–130)	18.9
toluene	9.51 (4.5–21.0)	3.59	69.4 (23–185)	25.4
ethylbenzene	1.61 (0.7–2.8)	0.48	3.2 (1.3–5.7)	0.8
m-,p-xylene	5.95 (3.7–14.5)	2.07	11.4 (2.6–22.9)	3.8
o-xylene	2.33 (1.1–3.7)	0.72	5.6 (2.6–9.7)	1.8
n-propylbenzene	0.57 (0.13–0.85)	0.14	0.4 (0.1–3)	0.1
3-,4-ethyltoluene	2.20 (1.5–3.2)	0.40	1.7 (0.8–3.8)	0.3
1,2,3-trimethyl-benzene	0.8 (0.6–1.1)	0.12	0.7 (0.2–2)	0.2

Table III. Variation in Fuel–Water Partition Coefficients for 31 Gasoline Samples[a]

	av K_{fw}	% dev	log K_{fw}	log S^{w} [b]
methyl tert-butyl ether	15.5	19	1.19	−0.26
benzene	350	21	2.54	−1.65
toluene	1250	14	3.10	−2.24
ethylbenzene	4500	13	3.65	−2.82
m-,p-xylene	4350	12	3.64	−2.85
o-xylene	3630	12	3.56	−2.79
n-propylbenzene	18500	30	4.27	−3.34
3-,4-ethyltoluene	12500	19	4.10	−3.34
1,2,3-trimethylbenzene	13800	22	4.14	−3.20

[a] Concentrations determined by GC/FID. [b] Aqueous solubility values taken from Brookman et al. (3).

Figure 2. Concentration dependence of measured fuel–water partition coefficients (K_{fw}) for benzene and toluene in gasoline.

These samples illustrated the changes in composition that may occur for a single brand and grade of gasoline and also indicated that MTBE was not a clear "marker compound" for any particular brand or grade.

Since MTBE is used as an octane enhancer, it may replace toluene or xylene in the fuel resulting in lower concentrations of those aromatic constituents. Conversely, the presence of this additive was also postulated to increase the water solubility of other components due to its high pure compound aqueous solubility of 48 000 mg/L (16). Concentrations of aromatic constituents in the water extracts for samples containing MTBE, however, were not significantly different (either higher or lower) than samples without this additive.

The concentrations of the aromatic constituents in a water extract reflect differences in gasoline composition. These appear to vary over as much as 1 order of magnitude. The components of highest aqueous concentration are the constituents of primary concern for regulation of gasoline releases to groundwater; i.e., benzene, toluene, ethylbenzene, and xylenes (BTEX). The range in concentrations of aromatic constituents in aqueous extracts, shown in Table II, reflects the range of saturated, equilibrium concentrations one may find in groundwater associated with gasoline releases.

Fuel–Water Partition Coefficients for Aromatic Constituents. Two techniques were used to evaluate partition coefficients. In one approach, K_{fw} values were calculated based on the results of 31 samples analyzed by GC/FID. This method requires analyses of both the fuel and water phases and may easily be applied to field investigations to provide data to estimate site-specific transfer of the BTEX constituents to groundwater. In the second approach, K_d's for ^{14}C-labeled solutes were measured in pure organic solvents, solvent mixtures, and fuels. These analyses focus specifically on factors that impact the distribution of components between the aqueous and complex organic phases.
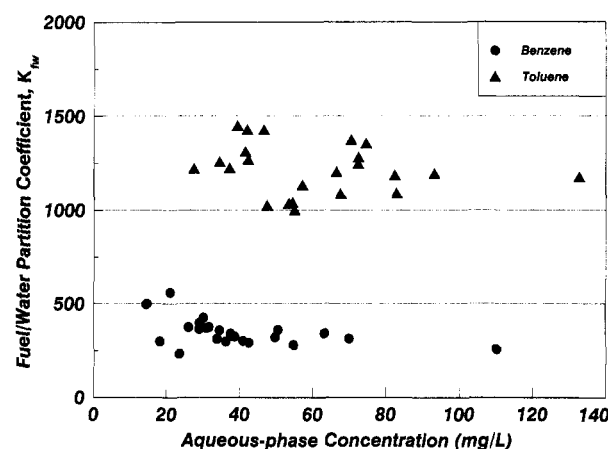
The K_{fw} values were expected to show greater variation than parameters like K_{ow} because of differences in the gasoline composition. Measurements of K_{fw} for 31 gasoline samples were examined to evaluate the variability in the coefficient (Table III). These results indicate the variability for estimating partitioning behavior. The reported measurements were based on the extraction protocol performed at room temperature (ca. 22 ± 1 °C) and a 1:20 fuel to water ratio.

The coefficient of variation for K_{fw} values for a given constituent measured in 31 gasoline samples varied between 11.5 and 30.0%, while for a given fuel the K_{fw} values for the 10 components varied over 2 orders of magnitude. This is rather consistent considering the wide variations in the compositions of the gasolines. To put this in per-

spective, log K_{ow} has been more precisely defined with only a three-component system and at fixed low solute concentration. It is frequently possible to estimate log K_{ow} with an uncertainty of no more than ±0.1–0.2 log K_{ow} unit (14).

Among the factors that could affect K_{fw} was the solute concentration. The relationship between K_{fw} and constituent concentrations was examined and is illustrated in Figure 2 for benzene and toluene. Generally, K_{fw} values did not show any significant trends with concentration. A somewhat higher K_{fw} value and a greater variability at low concentrations was noted for benzene, which is attributed to the coelution of nonaromatic hydrocarbon compounds during the gas chromatographic quantification of benzene in the neat gasolines. The effect of the presence of lower solubility, coeluting hydrocarbons on the estimate of K_{fw} for benzene would become more pronounced as the overall area percent of the benzene decreased. Toluene was generally in much higher concentration in the neat gasoline than most other components and eluted in a region of the chromatogram where less peak overlap was observed. The partition coefficient for toluene was not a function of concentration for these samples. Similar results were seen also for ethylbenzene and xylenes.

Sources of variability with the GC/FID technique included both compositional and analytical factors, in particular, coelution. However, the GC technique can be more easily applied as part of field contamination investigations if reasonable estimates of the variability of the technique are known.

The comparison of the distribution of constituents between the aqueous and organic phases is a function of the ideality of the organic phase. Since the composition of the organic fuel mixture may show considerable variability, the impact of composition on the partition coefficient

Table IV. Distribution Coefficients (K_d) for Selected Solutes as Determined by the ^{14}C-Labeled Solute Technique

solvent	av K_d	% Dev	log K_d	no. of detns
	Solute: Benzene			
MTBE	355	4.6	2.55	3
TCE	350	8.8	2.54	3
toluene	334	13.5	2.52	6
BTX mix[a]	319	8.6	2.50	3
benzene	299	7.4	2.48	3
75% BTX[b]	278	12.3	2.44	3
50% BTX[b]	272	3.8	2.43	3
xylenes	268	5.8	2.43	3
hexene	261	3.0	2.42	3
25% BTX[b]	233	2.2	2.37	3
gasoline	217	7.7	2.34	12
comb. mix[c]	209	10.8	2.32	3
hexane	184	13.4	2.26	6
alkane mix[d]	167	2.5	2.22	3
octane	162	8.5	2.21	3
diesel fuel	150	7.2	2.18	3
octanol	139	4.2	2.14	6
hexadecane	124	7.6	2.09	3
	Solute: Toluene			
gasoline	687	9.3	2.84	9
hexane	508	7.5	2.71	4
diesel fuel	484	27.3	2.69	6
octanol	462	4.3	2.66	5
toluene	398	26.6	2.60	8
isooctane	321	10.6	2.51	4
	Solute: Naphthalene			
gasoline	1509	11.4	3.18	7
diesel fuel	1183	27.0	3.07	6
toluene	1183	23.5	3.07	4
octanol	1039	12.2	3.02	12
hexadecane	821	41.5	2.91	3
hexane	658	46.0	2.82	3
isooctane	625	25.6	2.80	3
propylbenzene	549	16.9	2.74	4

[a]BTX mixture: benzene, toluene, mixed xylenes (33.3% each, v/v/v). [b]yy% BTX: yy% BTX mixture + $(100 - yy\%)$ alkane mixture. [c]Combined mixture: 40% BTX mixture + 40% alkane mixture + 10% MTBE + 10% hexene (v/v/v/v). [d]Alkane mixture: hexane, octane, hexadecane (33.3% each, v/v/v).

Table V. Comparison of Measured log K_{fw} Values

compound	GC/FID (^{14}C)[a]	API PS-6 ref gasoline[b]
benzene	2.54 (2.34)	2.39
toluene	3.10 (2.84)	3.02
ethylbenzene	3.65	3.54
m-,p-xylene	3.64	3.55
o-xylene	3.56	3.39

[a]This study GC/FID (^{14}C). [b]Brookman et al. (3).

aromatic and aliphatic solvents gave intermediate K_d values. Gasoline, a mixture of aromatic and aliphatic constituents, predictably gave an intermediate K_d for benzene.

By use of these data, general upper and lower bounds for the K_d for benzene can be estimated for complex fuel mixtures such as gasoline and diesel fuel. The partition coefficient measured by GC/FID for this gasoline sample was 285 (log K_{fw} = 2.45), which is approximately 0.1 log unit higher than that measured with [14]C. This is primarily attributed to the limitations in quantitation of benzene in the organic phase using the GC/FID resulting from possible peak overlap. The average distribution coefficient for benzene with ^{14}C was approximately 0.2 log unit lower than the average K_d measured by using GC/FID for the 31 gasoline samples.

For toluene, K_d values showed greater variability than observed for benzene, and gasoline did not have a partition coefficient intermediate between that observed for aromatic and alkanes. The K_{fw} for this specific gasoline sample, as measured by GC/FID was 652, which is lower than that for most other gasolines we studied. However, this value is within 5% of the average value measured by the ^{14}C technique.

Naphthalene K_{fw} was also higher for fuel mixtures than other solvents. The variability increases for the more hydrophobic constituents since they are more sensitive to small changes in the aqueous-phase concentration measurements using this technique. Naphthalene appears to be somewhat more soluble in mixtures like gasoline or diesel fuels than in single solvents. The K_{fw} for naphthalene was not measured by using GC/FID because accurate quantitation was not obtained in the aqueous phase with the purge and trap technique.

The K_{fw} values measured in this study provided a reasonable estimate of the partitioning behavior of specific constituents regardless of the gasoline composition. A comparison of K_{fw}'s for selected constituents obtained are presented in Table V. It should be recognized that the measured composition of the fuel and the aqueous phases may vary with the fuel-water volume ratio used, especially at low ratios when the fuel phase is likely to become depleted of the more water soluble constituents (19). At a fuel to water ratio of 1:20, depletion of the hydrocarbon constituents of interest from the fuel phase was not a problem.

The K_{fw} values reported by Brookman et al. (12) were lower by about 18–30% than the average result measured by GC/FID, but within two standard deviations of the average value. Their results, which indicated greater partitioning into the water phase or higher concentration in the organic phase, may have been due to differences in analytical and extraction protocols or gasoline composition.

Water-Soluble Blending Agents. The most water soluble constituent detected in some of the gasoline samples, MTBE, had no apparent effect on the aqueous-phase concentrations of aromatic compounds measured for these gasoline-water mixtures. The partitioning of MTBE was

estimates was evaluated. Previous studies have suggested that mixtures of structurally similar organic liquids form ideal solutions in the organic phase and the release of these constituents to air or water may be estimated by Raoult's law. This has been shown for mixtures of aromatic constituents like benzene and toluene, as well as saturated alkane constituents like hexane and octane (5, 6). Mixtures of alkanes and aromatic constituents show deviations from ideality that result in somewhat higher aqueous concentrations in the aqueous phase than predicted by Raoult's law. This nonideality will influence the distribution of solutes of interest from gasoline mixtures.

Distribution coefficients as measured by ^{14}C-labeled solutes in single solvents and solvent mixtures are summarized in Table IV. The K_{ow} values measured by this technique agreed with values reported in the literature (17, 18).

Benzene rapidly equilibrated, and the relative deviation for replicate analyses was generally less than 9%. The K_d's for benzene varied between 124 and 355 (log K_d's between 2.09 and 2.55) for various pure solvents and mixtures. Lower K_d values were measured for alkane solvents, including specific alkanes, alkane mixtures, and diesel fuel. Higher K_d's however, were measured for benzene in aromatic solvents, trichloroethane (TCE), and the gasoline additive MTBE. Benzene partitioning in mixtures of

Table VI. Solvent–Water Partitioning of MTBE and Methanol

solute	solvent	av K_d	rel dev, %	log K_d	no. of detns
MTBE	gasoline	15.7	4.3	1.19	6
methanol	gasoline	0.0051	0.7	−2.29	4
	toluene	0.0135	3.4	−1.87	4
	toluene/hexane	0.0069	1.5	−2.16	4
	hexane	0.0034	4.6	−2.47	4

not estimated from the data generated for the four samples containing this additive due to peak overlap and decreased FID sensitivity.

Separate experiments were performed by GC/FID to estimate K_{fw} for MTBE and to evaluate its effect on the partitioning of other constituents. A regular unleaded gasoline that did not contain oxygenated compounds was spiked with MTBE at concentrations as high as 11% by weight, which is slightly in excess of the maximum allowable concentration. Water extracts of the gasoline-blend mixtures were obtained as described earlier. The K_{fw} (or K_d) for MTBE was found to be 15.7 ± 4.3 (Table VI). The standard deviation for the measured K_{fw}'s was 0.05 log unit.

The partition coefficients for alcohols used as additives are less than 1. The distribution coefficient for methanol was measured with ^{14}C-labeled solutes and the distribution coefficient for gasoline was intermediate between that measured for toluene and hexane solvent phases.

These K_{fw} results can be compared with those reported by Grove (9) by calculating a solvent–water distribution coefficient based on concentrations, similar to K_{fw}, instead of ratios of mole fractions as reported. The solvent–water distribution coefficients for MTBE were 23.3 for benzene–water and 14.9–15.5 for hexane–water. The distribution coefficient for methanol between hexane and water was 0.002–0.004. These solvent–water partition coefficients correlate with the K_{fw} experimental results. A partially miscible cosolvent like MTBE concentrated in the solvent or fuel phase, while the completely miscible alcohols predominantly partitioned into the aqueous phase. The K_{fw} measured for MTBE of 15.5 was closer to the solvent–water partition coefficient for the hexane–water (14.9–15.5) system than for the benzene–water (23.3) system.

Since the aqueous solubilities of the oxygenated additives were so high relative to other fuel constituents, the possibility of a cosolvent effect existed. This effect would increase the solubility or partitioning of other fuel constituents into the aqueous phase. The concentrations of benzene and toluene measured in the aqueous phase in the presence of these additives showed typical analytical variations in concentration and were not enhanced at higher percentages of additives.

The solubility of a solute in an aqueous–cosolvent mixture is a function of the mole fraction of the cosolvent (oxygenated additive) in the aqueous phase. The mole fraction of oxygenated compound in the extraction experiments was a function of the volume percent of the additive in the fuel, and the fuel to water ratio used in the extraction. The fuel to water extraction ratio was less critical for the equilibrium concentrations of the less soluble hydrocarbon components since negligible amounts partition into the water and a large excess of fuel was present. The addition of oxygenated compounds to gasoline at a regulated maximum level of 10% for ethanol and *tert*-butyl alcohol would result in a volume fraction cosolvent in the aqueous phase of 0.005 (aqueous mole fraction of less than 0.002) for the 1:20 extraction procedure used in these experiments. Grove (9) measured an

increase in benzene solubility of ~18% when the ethanol mole fraction in water was approximately 0.025 compared to the benzene solubility in water. Therefore, with a 1:20 fuel/water ratio, a cosolvent effect is expected to increase benzene solubility by ≤2%; such an increase would be difficult to measure and would not be significant for field-scale applications. Assuming that the only source of alcohol was from the gasoline, an alternate water–gasoline extraction ratio of less than 1:1 would be required to show a measurable cosolvent effect for the alcohols. This situation corresponds to ≥50% residual saturation of the pore spaces by gasoline.

MTBE is not expected to show a cosolvent effect even at high fuel to water ratios. The distribution coefficient for benzene between MTBE and water was measured by the ^{14}C technique. The average K_d for benzene (355) was higher than measured for other solvents and solvent mixtures shown in Table V. Using MTBE as the solvent phase results in an aqueous concentration of MTBE near its solubility limit, significantly higher than would be released from a gasoline mixture containing 10% MTBE. More importantly, the high K_d suggests the aqueous phase would contain lower, not higher, aqueous concentrations of benzene in the presence of this component.

**Prediction of K_{fw} for Other Gasoline Components.** An average value for K_{fw} could be used to describe the partitioning into water of gasoline components (e.g., benzene, toluene, etc), which has been quantified in this study. For other gasoline constituents, the K_{fw}'s may be estimated from a regression equation. A least-squares regression analysis of the log of the fuel–water partition coefficient (log K_{fw}) and the log of the solubility (log S) was examined to determine the degree of correlation of those parameters. If they were highly correlated, the equation could be used to predict the K_{fw} for various constituents that were not measured in this study. Therefore, the aqueous-phase concentration of other components can be estimated given the average K_{fw} and the concentration in the fuel ($C_w = C_f/K_{fw}$).

Solubility may be used to provide an estimate for the partitioning behavior of a broader spectrum of gasoline constituents. One limitation of previous regression models was the caveat that the model was applicable to only the specific gasoline for which it was derived (12). The results reported in our study indicate that the K_{fw} may be more widely applied to estimate fuel–water partitioning for a range of fuel compositions, i.e., different brands and grades. The relationship between the log of the average fuel–water partition coefficient and the log of the solubility (S_i^w) was determined for MTBE and eight aromatic compounds: benzene, toluene, ethylbenzene, *m*-,*p*-xylene, *o*-xylene, *n*-propylbenzene, and 1,2,3-trimethylbenzene. The plot of the log K_{fw} versus log S_i^w is shown in Figure 3. These results may be compared with predicted ideal behavior of the constituents based on the assumptions that the average molecular weight ($\overline{MW}^o$) of gasoline ranges from 100 to 105 g/mol (see eq 4) and its density (δ) is 0.74 g/mL. The line for "ideal" behavior

$$\log K_{fw} = -1.00 \log S_i^w + 0.85 \qquad (7)$$

is plotted in Figure 3 and provides an excellent fit to the measured data. Thus, fuel–water partition coefficients for liquid solutes may be estimated by using reported values for aqueous solubilities; actual K_{fw} values for a specific fuel may, however, vary by as much as 30%.

In applying eq 7 to estimate K_{fw} values for fuel constituents that are solids, the correct solubility to be used is not that of the solid, but that of the super-cooled liquid
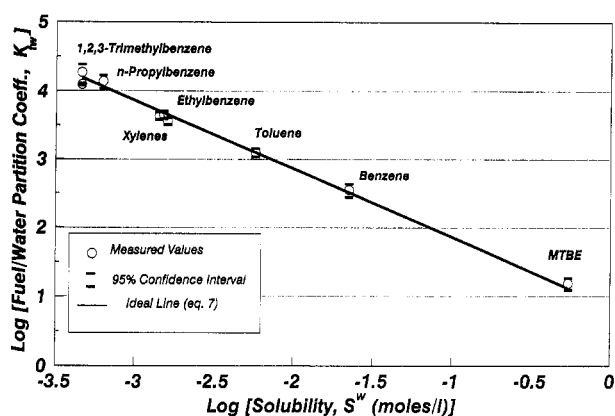
Figure 3. Relationship between fuel–water partition coefficients (K_{fw}) and aqueous solubility (S_i^w) for major gasoline constituents. The line shown is calculated by using eq 4 and assuming Raoult's law to be applicable; average molecular weight of gasoline was assumed to range from 100 to 105, and its density to be 0.74 g/mL.

(i.e., corrected for melting point). Chiou et al. (20) presented an analysis of the published data for the octanol–water partition coefficient (K_{ow}) and aqueous solubility for a wide range of liquid and solid solutes. They noted an inverse, log–log relationship, similar to that given by eq 7, but with a slope of −0.862 and an intercept of 0.71. Thus, a slope less than unity indicates that the measured K_{ow} values were systematically smaller than those expected based on ideal behavior. This suggests that if fuel–water partitioning data for a larger number of compounds with a much broader range in solubilities, especially solids, were considered, deviations from eq 7 might become evident. This aspect cannot be evaluated because the data presented in Figure 3 are all for liquid solutes.

Summary and Conclusions

Gasoline composition shows considerable variability. Aqueous extracts of gasoline show concentrations of major aromatic constituents like benzene and toluene which range over nearly 1 order of magnitude. The relationship between constituent concentrations in the fuel and water phases may be estimated by using partition coefficients. The K_{fw} is correlated to the solubility of the constituents and may be estimated by assuming ideality in the organic phase. Several sources of variability contribute to the errors in estimates of fuel–water partition coefficients. These include assumptions regarding mole fraction and nonideality in the organic phase as a result of the mixture of aromatic and aliphatic hydrocarbons. The GC/FID provides a simple tool to evalute the fuel composition that may be used for screening purposes, provided the program is adjusted to provide reasonable peak separation.

Registry No. MTBE, 1634-04-4; benzene, 71-43-2; toluene, 108-88-3; ethylbenzene, 100-41-4; m-xylene, 108-38-3; p-xylene, 106-42-3; o-xylene, 95-47-6; n-propylbenzene, 103-65-1; 3-ethyltoluene, 25550-14-5; 4-ethyltoluene, 622-96-8; 1,2,3-trimethylbenzene, 526-73-8; trichloroethane, 25323-89-1; hexene, 25264-93-1; octane, 111-65-9; octanol, 29063-28-3; hexadecane, 544-76-3; isooctane, 540-84-1; propylbenzene, 103-65-1; naphthalene, 91-20-3.

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